ECONOMIC GEOLOGY

VOL. XXXI NOVEMBER, 1936 No. 7

ALKALINE AND ACID SOLUTIONS IN HYPOGENE ZONING AT CERRO DE PASCO.[1]

L. C. GRATON AND SAMUEL I. BOWDITCH.

OUTLINE.

Page

Introduction 651
The Local Facts 653
The General Setting 653
The Zoning of Rock Alteration 655
General Features 655
Alterations of the Igneous Rocks 655
Feeble Phase 656
Moderate Phase 658
Intense Phase 659
Alteration of the Excelsior Rocks 665
Zonal Distribution of the Sulphides 667
Relations of Zoning in Rock and in Ore 670
Nature of the Solutions 674
Present Status of Opinion 674
Interpretation at Cerro de Pasco 678
Alkaline Solutions Formed Moderate and Feeble Zones 678
Acid Solutions Later Formed Intense Zone 679
Cause of Change from Alkaline to Acid 683
Locus and Conditions of Acid Generation 687
Vertical Range 691
Metallogenetic Significance 695
Résumé 696

INTRODUCTION.

DESPITE the constantly accumulating evidence in support of the view that most ore deposits of sulphidic character are of magmatic origin, that hypothesis cannot be accepted with safe complacence

[1] Presented before the Society of Economic Geologists, New York meeting, Dec., 1935. Published with permission of the Cerro de Pasco Copper Corporation.

nor successfully defended against every challenge until more unified opinions are held by its proponents on several of the most crucial matters involved in that origin. So long as the " experts " disagree radically on such vital questions as whether the mobile agent of transport was of magmatic or mixed derivation, was molecular or colloidal, liquid or gaseous, acid or alkaline, and as how this mobile agent effected its supposed separation and escape from the magma, doubters will still have basis for insisting that the hypothesis rests on a lot of vague assumptions and speculations relating to materials and processes of which little is known.

This vulnerable and unsatisfactory situation, as usual, exists chiefly through lack of sufficient definite *facts* acceptable without ambiguity. The great sulphide deposits and the associated wall rock alteration at Cerro de Pasco, Peru, as now developed, shed clear and unequivocal light upon the relations and the sequence of alkalinity and acidity in the solutions responsible for them. And from these certain facts, apparently inescapable inferences may be drawn regarding other conditions of these solutions.

This paper is built upon detailed geological study of the district, carried on systematically and continuously by the Cerro de Pasco Copper Corporation for more than 15 years. Many have contributed to its underpinning, and several of these have helped to further the specific ideas that are its major text. We are particularly indebted to Prof. D. H. McLaughlin, for many years Chief Geologist of the Corporation, to Mr. W. F. Walker, his successor in that office and a student of Cerro geology since 1918, to Mr. J. O. Hosted, former member of the geological staff and now Assistant Superintendent of the Cerro Division, to the late Dr. R. D. Harvey, former petrographer of the Geological Department, and to Mr. O. C. Schmedeman, recently senior geologist of the Cerro Division. Our thanks are also due to Mr. R. C. Philpott, Superintendent of the Cerro Division and to Messrs. Harold Kingsmill and Raymond Spilsbury, respectively General Manager and Assistant General Manager of the Corporation, for helpful discussions of the practical aspects of these geological conclusions. To the officers of the Corporation we are indebted for

permission to put on record these facts and interpretations. Dr. E. S. Larsen, Jr., has generously given of his expert knowledge to aid us in some of the mineral identifications, and Dr. E. B. Dane, Jr., has helped with his skill in the photography.

The present geological staff at Cerro de Pasco is continuing with the investigation of this problem as a part of its regular tasks. This paper is thus a progress report by the present authors, respectively consulting geologist, and former senior geologist of the Cerro division. It emphasizes the features that are of general genetic significance; no deliberate effort is made to record their direct applications to ore-finding in this particular district.

THE LOCAL FACTS.

The General Setting.

An adequate summary of the geology and ore deposits of the Cerro de Pasco district has recently appeared.[2] Therefore, only those features which directly affect the present question will be mentioned here.

Along the great Cerro Fault cutting northerly through the heart of the district, Paria limestone (Triassic-Jurassic) on the east overrode the Excelsior phyllites and impure quartzites (Silurian or older) which constitute the great basal formation of all this high Andean region. In (probably) Early Tertiary time, an underlying magma of quartz monzonite exploded a vent through the Excelsior rocks so close to the fault that at the level of the present erosion surface the eastern margin of the vent is essentially tangent to the fault. This steep-walled explosion throat of elliptical plan, roughly 9,000 feet by 8,000 feet in dimension, is now occupied by three kinds of material: the compacted explosion-debris which fell back into the vent (Rumiallana agglomerate), composed largely of fragments of Excelsior rocks and of comminuted quartz-monzonite porphyry; an intrusive breccia (locally called the Lourdes fragmental), consisting of Excelsior fragments in a dominant matrix of (mainly) non-brecciated

[2] McLaughlin, D. H., Bowditch, S. I., and others: Copper Resources of the World. 16th Intern. Geol. Cong., vol. 2, pp. 516–527, 1935.

quartz-monzonite porphyry; and an irregular intrusive mass and numerous dikes of normal quartz-monzonite porphyry.

Beyond doubt, the volcano which formed this vent built up on the then-existing surface a debris-cone of substantial proportions. Subsequent erosion, however, has destroyed all trace both of the local topographic eminence and of the more distant beds of tuff that must have flanked the steeper parts of the cone. It is, therefore, impossible to determine how far the present erosion surface lies either below the summit of the cone or below the pre-volcano surface; but from the facts mentioned it would seem justifiable to guess that the present surface is some hundreds of feet, at least, below the pre-vent surface, and perhaps two or three thousand feet as a minimum below the crest of the debris cone.

Mineral-forming activity that succeeded the production and filling of the vent was concentrated chiefly near its eastern and southeastern margins. In addition to an enormous elongated replacement body rich in pyrite, which formed along the joint locus of the eastern side of the vent and the great Cerro fault, three major structural types of hypogene deposits resulted. These are: (1) irregular separate replacement masses of copper, silver, and lead-zinc ores in the main pyrite body; (2) mantos of silver and lead-zinc ores in the Paria limestone to the east of the pyrite body; and (3) definite veins along east-west fractures that cut the vent-filling near its eastern margin and in part continue into the pyrite body, and other veins that cut the Excelsior rocks just south of the vent. These veins, carrying pyrite and enargite as principal sulphides, have been the largest producers of hypogene copper up to date. Oxidation in the district varies in depth from a few feet to several hundred, but averages around 150 feet; supergene sulphides are important 200 feet deeper, but have no economic significance below a maximum depth of 500 feet.

The east-west copper-bearing veins in the Excelsior rocks and in the vent filling best disclose the nature of the mineral-forming solutions and therefore are principally considered at this time. The lead-zinc and pyritic silver ores have not been studied as intensively as have the copper ores, and for want of space are

omitted from this discussion, but it is not believed that they materially alter the picture here presented. On the copper veins, development has attained a depth of 2,100 feet; the uppermost third of that distance has now been largely extracted, the middle third is the present site of active stoping and the lowest third is now being opened up for future production.

The Zoning of Rock Alteration.

General Features.

Three phases of alteration are recognizable in the silicate rocks in which the veins lie, and these phases are so distributed in relation to one another and to the fracture channelways as to determine a definite zonal arrangement. A feeble phase, mostly far removed from ore, is marked by the production of chlorite, calcite and epidote, with scanty pyrite; a moderate phase, which abounds in the general region of mineralization but is rarely in contact with ore, includes sericite, pyrite and quartz as the chief new minerals; and an intense phase, almost invariably close to ore, which, where complete, converts the rock to an aggregate of quartz, pyrite, kaolin (dickite), and alunite. It should be emphasized that the complete development of this last phase, with the utter destruction of sericite, is rarely attained; generally more or less sericite is also present. Each phase grades into the next, so that no sharp boundaries between them can be drawn.

Alteration of the Igneous Rocks.

All of these phenomena of alteration are most clearly manifest in the quartz-monzonite porphyry and related fragmental varieties, whose character in the fresh condition is well known and in which there is no chance of confusing these hypogene hydrothermal effects with those of prior regional metamorphism as in the Excelsior rocks. Therefore, consideration is first given to the nature and distribution of alteration in the rocks of the vent filling.

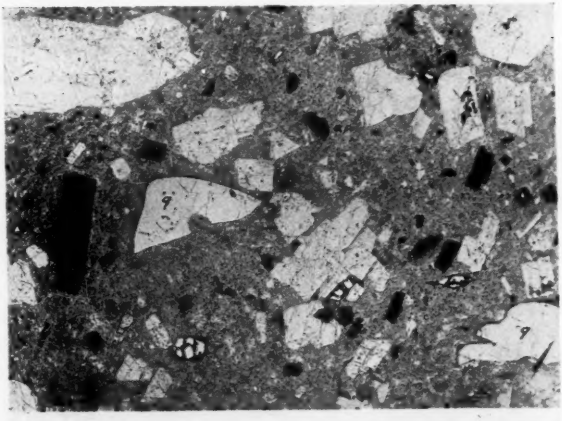
The fresh porphyry is of gray color with occasional good-sized phenocrysts of orthoclase, plentiful smaller phenocrysts of plagio-

clase (30–35% An), numerous plates of dark biotite, occasional hornblende crystals, and sparse resorbed units of quartz in a microcrystalline groundmass of quartz, orthoclase and subordinate plagioclase (Fig. 1). Apatite, titanite, rutile, zircon, magnetite and ilmenite are accessory minerals; apatite is particularly noteworthy, with some of its grains attaining the dimensions of phenocrysts.

Feeble Phase.—The first of the pyrogenic minerals to show attack is the titanite, which has broken down to the characteristic framework of rutile enclosing quartz and in some cases calcite (Fig. 1). In slightly more altered rock, the biotite has altered more or less completely to light green chlorite showing "ultra-blue" interference colors, probably pennine; and in slightly more advanced alteration, the chlorite has changed in turn to muscovite or coarse sericite; as is so common in such alteration of biotite, both the chlorite and the muscovite form "unit pseudomorphs"[3] after the dark mica, and both contain granules and tiny stubby crystals of rutile formed from the titanium content of the biotite. The hornblende breaks down to quartz and sericite, with the original outline preserved by tiny rutile crystals. Calcite and some epidote have started to form in the plagioclase phenocrysts, which may also contain scanty wisps of sericite aligned along the cleavage directions of the feldspar. The groundmass feldspar has altered sparingly to epidote, calcite, and rare siderite. The quartz, orthoclase, and apatite of the rock are essentially immune in this phase.

This incipient phase of alteration, which is closely analogous to feeble propylitization, is widespread. It may reach so far from any known channelway of importance that the means of ingress of the solutions which accomplished it there may not be evident. On the other hand there is in many places no room for doubt that this phase of alteration bears a definite positional relationship to the fracture-channelways now occupied by the veins;

[3] Those pseudomorphs in which both the external form and the internal crystallographic structure of the protosome are preserved—inherited—by a single identically oriented individual of the metasome.



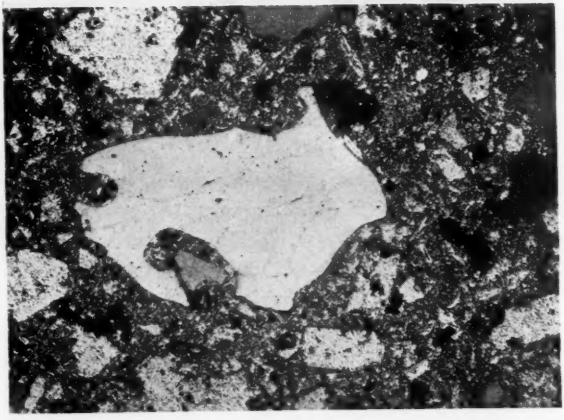


FIG. 1 (top). Fresh quartz-monzonite porphyry. Phenocrysts of quartz (q), biotite (black), plagioclase, and apatite (ap), in microcrystalline groundmass of quartz and orthoclase. Skeleton crystals are altered titanites. Plain light. × 15.

FIG. 2 (bottom). Sericitized quartz-monzonite porphyry. Former plagioclase phenocrysts are now a felt of sericite, in a groundmass of quartz and sericite. Dark patches are pyrite and holes. ×-nicols. × 25.

convincing proof of this may be found both in the gradual fading out of this alteration into fresh rock with increasing distance from a given vein and also, in the opposite direction, in the gradual increase in the quantitative importance of this phase of alteration and its gradual change to the second or moderate phase which latter always lies still closer to the veins. Nevertheless, this phase of alteration has never been found nearer than 100 meters to an ore body, nor even close to a strong vein of barren pyrite.

Moderate Phase.—Closer to vein or ore body, pyrite and sericite become abundant (Fig. 2). The common order of surrender to sericite attack is: chlorite from the original biotite, plagioclase phenocrysts, spherulites in the groundmass, and groundmass feldspars. The biotite and hornblende are by now completely destroyed, but their former individuals are clearly indicated by the unit pseudomorphs of sericite and by the tell-tale rutile. In the outer portions of this zone, the calcite, chlorite, and epidote of the feebler phase are seen to have been attacked, and farther inward where this moderate phase is well advanced, the calcite and chlorite have been quite destroyed. Pyrite forms notably in what were the biotites, as well as in the iron oxides and hornblendes, but also replaces the other silicates with little discrimination. Part of the groundmass quartz has undergone enlargement either by introduction of new silica or by utilization of that which the pyrite and sericite have displaced; small patches of clear micromosaic quartz thus appear in the old groundmass. On the lowest (2,100) level, some of the quartz developed in the groundmass tends to form large, rather vague grains approximately 0.1 mm. across, which are peppered with residual sericite, whereas on the upper levels the new quartz is clear, and rarely larger than 0.02 mm. Before sericitization has become complete, near the inner margin of this zone, the apatite has been completely destroyed, and in most such instances leaves no trace of its former presence. A few areas having the shape, size, and distribution of the original apatite crystals are nests of interlocking grains of a mineral that probably belongs to the alunite group, for in other

respects than slightly higher index and slightly lower birefringence its optical properties are similar to ordinary alunite, and these areas are commonly rimmed by another alunite mineral of still higher index. Various hydrous phosphates are known in the alunite group and it seems reasonable to assume that these alteration patches from apatite belong in that category. Small irregular bunches of barite formed at this stage. At the inner margins of this zone where its effects are most intense, every important initial mineral has been destroyed except the quartz; the embayed quartz phenocrysts and the small zircon crystals alone are unchanged. Nevertheless, the initial textural pattern of the rock is commonly preserved with striking fidelity by the alteration products.

In the portions of the crater filling most thoroughly opened by the mine workings, *i.e.* in the general ore-bearing region, this dominantly sericitic alteration is the most abundant type. Where strong veins are only a few tens to a few hundreds of feet apart, this moderate phase of alteration has completely excluded, or expelled, the feebler phase; but where the veins are narrower and weaker or are far enough apart, the feeble phase of alteration appears in the mid-region between the veins and separates the sericitic zone centered on one vein from that centered on the next. Veinwards, this moderate alteration may occasionally reach the actual margins of the sulphide veins that are low or barren in copper, but it almost invariably begins to give way to the intense type of alteration before reaching those veins or portions of veins that constitute copper ore shoots.

Intense Phase.—As a rule, the commercial copper ore of the veins is adjoined by wall rock in which still further alteration has taken place. This is marked by the destruction of sericite and by the development of alunite, kaolin (dickite), zunyite, zoisite, and an unknown mineral, as well as of further quartz, pyrite, and epidote; in a few localities, tiny grains of tourmaline occur, commonly enclosed in pyrite. These minerals do not form simultaneously nor do they exhibit a fixed sequence; from place to place their relative order varies, this being especially true for

alunite and dickite. In general, however, zunyite and the unknown species were formed after the sericite and a little before most of the dickite and alunite; the period of alteration generally closed with deposition of the latest quartz.

The zunyite occurs in the characteristic triangular sections, with tetrahedral cleavage and concentric zoning notable (Fig. 7). The unknown mineral is colorless, isotropic, and of index about 1.65. Epidote forms good-sized clear grains of gloriously brilliant polarization colors, in contrast with the turbid aggregated patches of granules present in the feeble phase. Similarly clear is the small amount of associated zoisite. The epidote and zoisite here formed in part ahead of the alunite, which builds composite rosettes upon clusters of their grains; not always, however, is the sequence clear.

The first of the kaolin and alunite developed at the expense of the sericite which had replaced the feldspar phenocrysts and the biotite and hornblende; and they then developed in the groundmass as the process was carried further.[4] The kaolin possesses the optically positive character diagnostic of the hydrothermal variety, dickite, and tends to form tiny but perfectly recognizable plates. The alunite exhibits two major habits, each with two or more subdivisions. On the upper levels the commonest occurrence is in the form of acicular grains, elongated parallel to the base. On the lower levels the grains of this variety are thicker and appear in thin section as broad blades (Fig. 5). The index of this sub-type is slightly higher, and the birefringence lower than of the acicular type. A second variety is strongly rhombohedral; and often exhibits marked zoning in which the core and a surrounding layer of still higher index are enclosed in accordant optical orientation by the more acicular alunite, which possesses a much lower refringence and higher double refraction than the two inner varieties (Fig. 8). Especially on the deepest level, this high index rhombic type is found also as ragged grains scattered sparingly through the rock. The increase in index of

[4] Alunite and kaolin (dickite) are never seen directly replacing fresh feldspar; and in fact are always separated from fresh feldspar by the full width of the sericite zone.

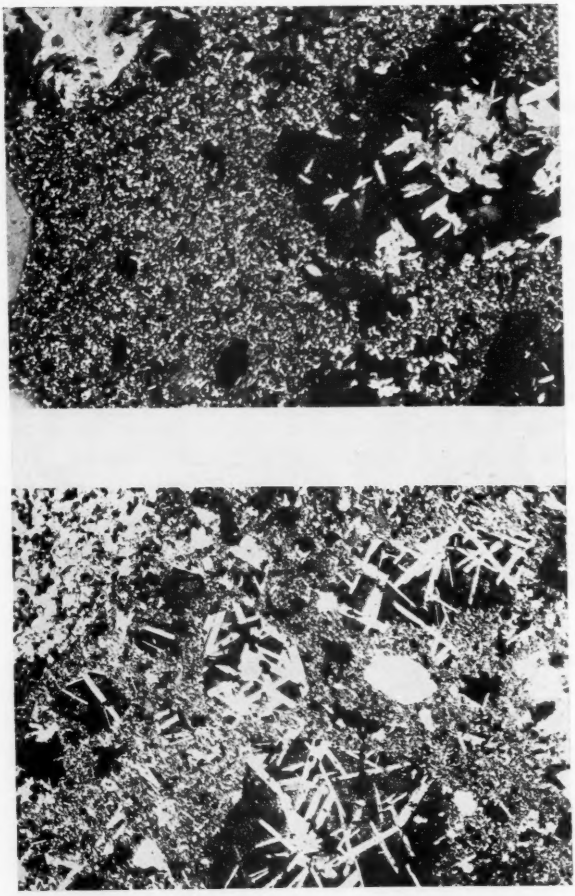


FIG. 3 (top). Quartz monzonite porphyry completely altered to quartz, fine-grained kaolin (dickite) and alunite; fine-grained dark areas are kaolin pseudomorphs after plagioclase, and light colored blades are alunite. The groundmass is quartz and some dickite. ×-nicols. × 25.

FIG. 4 (bottom). Agglomerate completely altered by intense phase. White blades, alunite; fine-grained dark patches, dickite; large white areas, quartz fragments; groundmass quartz and some dickite. Coarse-grained area in upper left is a fragment of Excelsior quartzite. ×-nicols. × 25.

refraction and accompanying lowering of the birefringence is probably due to an increase in soda at the expense of potash.[5] Clean, fresh, euhedral alunite may occur in the midst of kaolin masses (Fig. 3, 4), but elsewhere the core of each alunite crystal may be rotted to kaolin, with only a residual marginal rim of the original material, presumably of more resistant composition. Kaolin may attack the sericite of the old feldspars without any sign of alunite; or alunite may develop first and later be attacked by kaolin which thence spreads out like a fungus to consume part or all of the remaining sericite (Fig. 6).

Quartz in varying proportion may accompany the development of alunite and kaolin. In areas of intense silicification, the quartz that has replaced the preceding inheritor of the initial biotite is strewn with the still-resistant granules of rutile while that which has replaced what once was the feldspar phenocrysts is clear; a little kaolin may occur between the grains of quartz. The secondary quartz that forms in the groundmass is relatively fine-grained, notably mosaic in texture, and of pronounced turbidity because of what appear to be countless tiny (refractory) residues. Even in such thoroughly silicified material, which evidently represents the extreme stage of rock alteration, the igneous texture has rarely been obliterated beyond detection. More commonly it is still surprisingly plain: appropriately-shaped arrangements of rutile granules mark former sphenes and biotites, the quartz phenocrysts and the crystals of original zircon survive, and not infrequently the feldspar phenocrysts are neatly revealed by the sharp contrast in grain-size of the alteration product respectively within and outside their former boundaries (Fig. 9, 10). It is clear that this silicification is the result, not merely of the leaching of alkalies and alumina, which would leave a porous skeleton of quartz, but also of an actual introduction of silica from the solutions so that the rock is dense and solid.

Alunite and dickite, which are the most diagnostic representatives of this zone of alteration, have never been found more

[5] Larsen, E. S., Jr., and Berman, H.: The Microscopic Determination of the Non-Opaque Minerals. U. S. Geol. Surv., Bull. 848, p. 219, 1934.

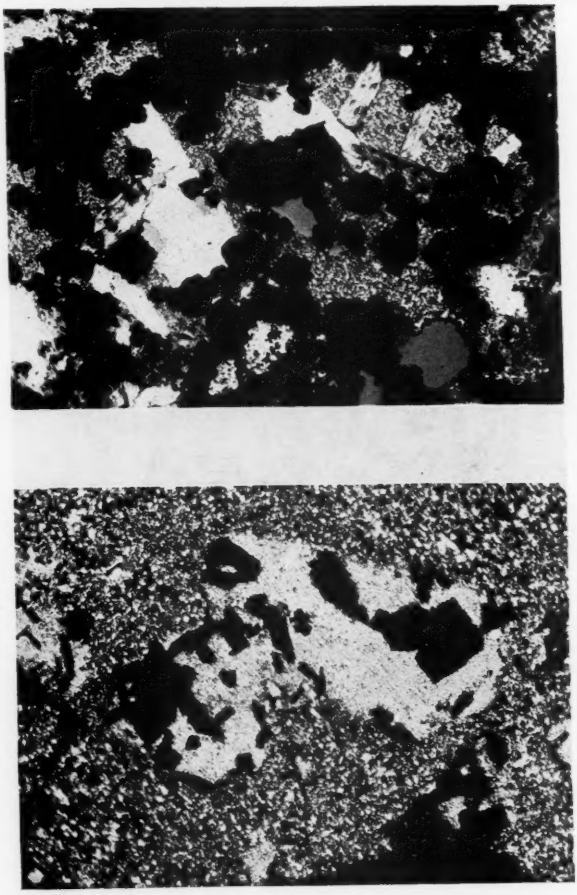
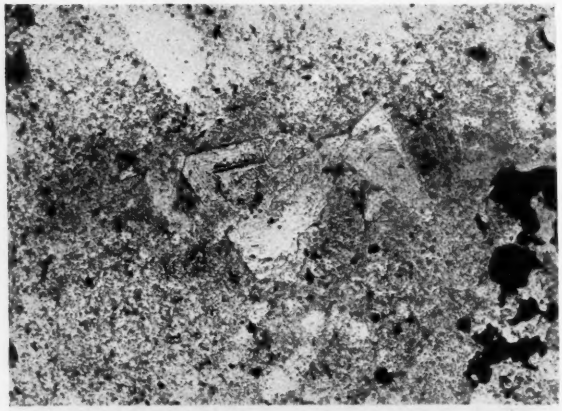


FIG. 5 (top). Alunite, broad blades, replacing sericite. Black is pyrite. X-nicols. X 80.

FIG. 6 (bottom). Dickite pseudomorphs after alunite which had replaced sericite of former plagioclase phenocryst. Black square is pyrite. X-nicols. X 45.



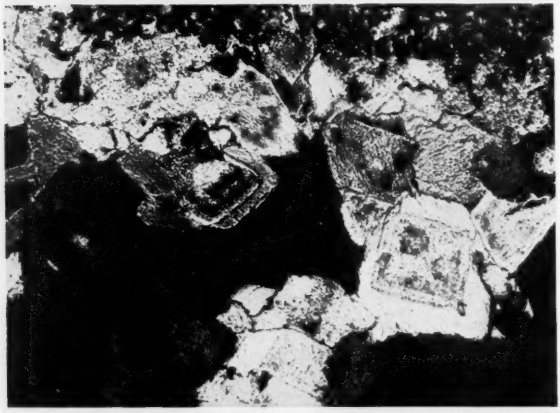


FIG. 7 (top). Zoned crystal of zunyite in sericitized and pyritized groundmass. Plain light. × 85.

FIG. 8 (bottom). Zoned alunite, with high index rhombic core surrounded by lower index blady variety. ×-nicols. × 120.

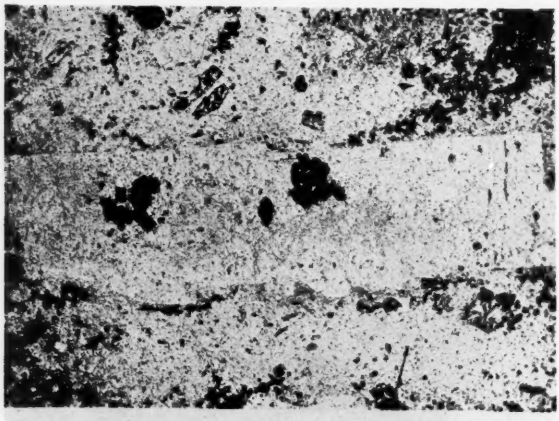
than a hundred feet distant from enargite deposition, and they usually die out at a much smaller distance measured in a direction normal to the plane of the vein. In general, their width of distribution is greatest marginal to the strong, rich veins and correspondingly low along subordinate stringers. Where a copper ore shoot in a vein plays out at the ends to lean pyritic material, the width of this alunite-dickite zone appears to decrease and finally to pinch out not far beyond where the good copper values cease. It should be made clear that this intense zone is rarely completely developed; as a rule more or less sericite is still present.

Alunite and dickite persist to the deepest level yet opened, which is approximately 2100 feet below the present surface. In certain veins on that level, coarsely crystalline pink alunite, first mistaken for rhodochrosite, occurs *within the vein proper,* mostly in vuggy places, perched upon and also intergrown with coarse grained enargite. Detailed sampling for the purpose has not yet been sufficiently completed to establish the *quantitative* distribution of these minerals with depth. The impression is gained that on the 2100 level the alunite, at least, is as widely spread but less abundant than on the upper levels; in other words, the alteration is less intense.

Alteration of the Excelsior Rocks.

Alteration in the Excelsior formation is in many ways similar to that which has affected the porphyry. The rocks consist chiefly of quartz and sericite, with low calcium and magnesium. In them, therefore, the feeble phase of alteration found in the igneous group is virtually absent, both because they lack the constituents to form the calcite, epidote, and chlorite characteristic of that phase and because they lack the pyrogenic silicates, chiefly feldspar and biotite, which are so easily susceptible to replacement by those characteristic alteration minerals.

The moderate phase or intermediate zone of alteration is also less strikingly developed in these metamorphosed sediments than in the porphyry because the chief components of these rocks,



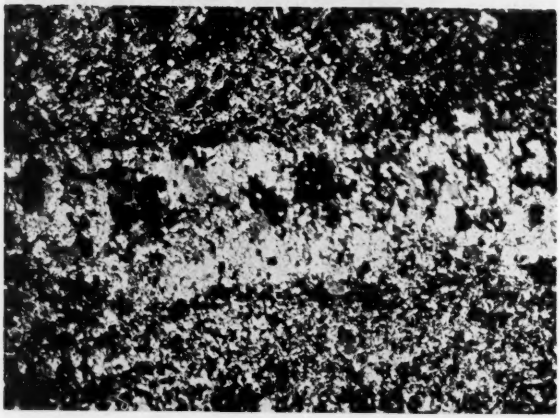


FIG. 9 (top). "Ghost" of plagioclase phenocryst in silicified quartz-monzonite porphyry; ragged groups of high index (dark) grains are epidote. Former biotites or hornblendes outlined by rutile, just above "ghost." Black areas are pyrite. Plain light. ×20.

FIG. 10 (bottom). Same as Fig. 9, but with crossed nicols to show that plagioclase has been completely converted to an aggregate of quartz grains.

quartz and sericite, being the same as the characteristic products of the moderate zone, would be stable in it. The principal evidence of the moderate phase is, therefore, the introduction of pyrite; but quartz and sericite, formed along small to microscopic fractures across the foliation, are also plainly products of this stage of the process. The beginning of bleaching is also noted; the quartzitic members are naturally rather light colored, but most of the more sericitic layers are initially dark because of a highly disperse graphitic pigment; this carbonaceous material tended to be partially removed where solutions of the character that yielded the moderate phase of alteration have penetrated.

Close to the copper-bearing shoots, the intense phase of alteration developed but little less effectively than in the porphyry, for the plentiful metamorphic sericite of the phyllites and quartzites went over to alunite and dickite with about the same readiness as did the hydrothermal sericite of the igneous rocks. Clear, coarsely crystalline epidote was also introduced, just as in the intense zone in the porphyry; some of it preceded alunite and was plainly attacked thereby, but in at least one place crystals of alunite were marginally replaced by clear epidote which is oriented in optical parallelism with the alunite. Zuynite is also developed, though apparently to a much lesser extent than in the igneous rocks. Immediately adjacent to the ore shoots, the rock is quite thoroughly recrystallized to quartz, alunite, dickite, and epidote, and is almost invariably bleached. In a few specimens is seen the same unknown isotropic mineral as found in the corresponding zone in the rocks of the vent. Intense silicification, to a product containing little else than quartz and pyrite, may likewise occur in intimate contact with ore. In these more extreme phases of alteration, the schistose texture of the rock is nearly or quite lost.

Zonal Distribution of the Sulphides.

In a much more indefinite manner, the sulphide minerals also display a systematic distribution that may be designated as zoning; but the placing of the zones, and the controls of such placing are not wholly the same as for the zoning of the rock alteration.

The distribution of pyrite away from the veins has already been considered. It is at most places the only sulphide that gets definitely outside the immediate vicinity of the fracture channelways and into the wall rock; its occurrence in this manner is governed by the same general controls that determined the other products of rock alteration, and in the three zones pyrite is scanty in the feeblest, and decidedly more plentiful in the moderate and the intense zones. Pyrite is also the dominant sulphide of the vein-stuff proper. At many places strong veins consist almost wholly of pyrite, with interstitial quartz so subordinate that it is ordinarily recognized only in microscopical preparations. Where the copper ore shoots occur pyrite is still plentiful; but it invariably increases as copper values decline, and it is evident that this is in considerable part due to the fact that the dominant copper mineral, enargite, has vigorously attacked and replaced the pyrite. It is therefore possible to regard a part of the pyrite as having been driven by enargite from central places out into more distant terminal portions of the veins in much the same way that sericite of the intermediate phase of rock alteration drove earlier-formed calcite and chlorite out to more peripheral positions, though there is no indication of the quantitative importance of such displaced pyrite. Some of the latest pyrite, however, is later than the enargite.

The economically important copper shoots, as already implied, are those places in the veins where a sufficient amount of enargite has been deposited; in the wholly subordinate gangue, quartz greatly outweighs barite and epidote. The stope-length of individual shoots varies from the minimum that will justify stoping up to hundreds of feet; but between and beyond the shoots in any vein, lean or barren pyritic material constitutes the vein-stuff. In some of the most productive veins, the enargite shoots do not fade at their ends directly into barren pyrite but give way first to pyrite associated with a somewhat scantier development of tennantite-tetrahedrite and subordinate galena and sphalerite before the essentially barren pyritic portions are reached; these places are likely to be noticeably vuggy, and in some of the openings

crystals of barite are present, also patches of a white clay-mineral, possibly dickite or allophane, so incoherent when wet as to merit the nickname "cold cream."

As a matter of fact, the name enargite has been used thus far in this paper to stand not only for that mineral but also for the closely similar and intimately related variety, luzonite. The latter, so plentiful in the copper-ore pipes within the great pyrite body to the east, is, in the veins, almost invariably greatly subordinate to enargite. The two appear to be of essentially contemporaneous deposition and prefer to form in intimate contact.

Tennantite (somewhat antimonial) is closely associated with the enargite, but except very locally is much less abundant and is generally a little later. It is the principal silver carrier of the veins. With it is often associated a little chalcopyrite.

Marcasite, absent in the altered rock walls, occurs sparingly in the copper shoots. It appears to be, in the main, about contemporaneous with the early pyrite. A very little of the marcasite in the veins (much less than in the lead-zinc shoots farther east) shows the peculiar "lamellar" structure similar to that found by Turneaure so commonly in the tin ores of Llallagua;[6] we believe such marcasite replaced an earlier sulphide having a dominant platy cleavage, but we have found no residues of frankeite or of pyrrhotite (or other mineral) which could account convincingly for this Peruvian marcasite structure as he did so clearly for the Bolivian.

Locked within solid grains of pyrite and more rarely of enargite, occasional fair-sized single plates of covellite appear. The habit is entirely unlike the usual felty covellite of supergene formation, and the association likewise makes a superficial origin extremely improbable. Notably crystalline plates of early covellite believed to be hypogene also occur in the enargite ores of Butte[7] and in the enargite and luzonite-bearing deposits at Kennecott.[8]

[6] ECON. GEOL., vol. 30, plates on pp. 43–56, 1935.

[7] *Cf.* Graton, L. C., and Murdoch, Joseph: Am. Inst. Min. Eng. Tr., vol. 45, pp. 50–51, 1914.

[8] Bateman, A. M., and McLaughlin, D. H.: ECON. GEOL., vol. 15, p. 37, 1920.

Relations of Zoning in Rock and in Ore.

The geometrical picture may now perhaps be clarified by a brief recapitulation which ties together the disposition of wall-rock alteration and the zoning in the veins.

The zoning here discussed is developed on a substantial scale; it affects a region thousands of feet in both horizontal dimensions. The reason for this size is that within the area so affected are many veins which collectively and cumulatively contributed to the zoning. As a matter of fact, the primary structural element or unit for all the zoning is the individual fracture channelway which in time became a single vein. If there were only one such vein in the district, it would probably show a zoning of alteration of the rock in its neighborhood, and a zoning also of the sulphides in the vein itself. The essential features of the mechanism may be readily visualized by considering, in somewhat idealized fashion, what would result in such a highly simplified case.

It is inescapable that the new minerals in both wall-rock and vein are products of deposition or reaction by the solutes that ascended mainly along the fracture and thence "soaked" out into the walls. In the beginning of this process, it is probable that the calcite, chlorite, and epidote that characterize the feeble phase of rock alteration were first developed immediately adjacent to the fracture and gave way quickly outward to fairly fresh rock; at this stage, pyrite may have been starting to deposit within the fracture space. Continued ascent of solution and farther-reaching lateral soaking extended the width of the feeble-stage zone and simultaneously began to attack its inner edge by the replacing deposition of the new mineral, sericite, better adapted to the now higher temperature to which the immediate walls of the fracture had become heated. In other words, the first feeble zone was displaced outward by the beginning of growth of a new phase of alteration which may be called the moderate zone. Pyrite continued to deposit in the vein and now to get out also into the near-by walls. Continuation of this activity caused progressive widening of both zones, which necessarily involved a

still farther driving outward of the feeble zone, while still more pyrite and gangue formed in the vein proper.

The final step of rock alteration was the conversion of the inner part of the sericite zone into the minerals of the center-most or intense zone, namely, alunite, dickite, zunyite, etc. together with quartz. It is not clear whether this third zone (acting analogously to the second when that was the center-most one) forced the moderate and the feeble zones still farther outward, or whether, instead, it merely destroyed and took the place of the inner part of the moderate zone without moving the outer boundaries of the moderate and the feeble zones. The evidence of mineral sequence indicates that the enargite, luzonite, and tennantite, which are the characteristic minerals of the copper ore shoots, were depositing in the vein at the same late time that the alunite, dickite, etc., were developing immediately alongside in the walls.

When finally finished, the single, ideal vein and its surrounding country rock would look about like this:

(*a*) An enargite-pyrite ore shoot occupying the central stretch of the vein; enveloping this, and approximately coincident with it along the strike of the vein, a relatively narrow sheath of the alunite-dickite-quartz alteration.

(*b*) Where the enargite declines toward the ends of the enargite shoots, its place is often taken by tennantite, sphalerite, and galena, as well as vuggy barite and a soft clay mineral. This combination may be regarded as constituting an indefinite "intermediate zone" of the vein sulphides, but such an interpretation is somewhat complicated by the fact that, in the enargite shoots themselves, tennantite may replace enargite to some extent, and galena and sphalerite form tiny late veinlets. This intermediate zone occurs about where the alunite-dickite alteration pinches out to zero width and the sericite becomes tangent to the vein.

(*c*) The end portions of the vein *are* end portions because the fracture was there becoming a weaker, less effective channelway; therefore, these end portions carried less solution and less heat

than the central stretches of the vein. The conditions that caused deposition of enargite centerward and of the scanty intermediate group, tennantite, sphalerite, and galena, did not extend to these end portions, and pyrite was the only sulphide deposited there. The wall rock adjacent to these pyritic terminal portions of the vein shows the characteristic sericitic alteration of the moderate zone; toward the center stretches of the vein this sericite zone departs or spreads away from contact with the vein so as to surround the center-most zone of alunite and dickite.

(*d*) As the outermost shell surrounding the whole, never getting in contact with important veins whether commercial or pyritic, is the feeble calcite-chlorite phase of rock alteration.

The true situation differs from this simplified and idealized concept chiefly in that there are many sub-parallel veins instead of only one. And these are located sufficiently near together so that some of their zones "interfere." Therefore, between two veins of wide spacing there may be a strip of feeble zone; between veins somewhat more closely spaced, their moderate zones may coalesce, thus excluding from between them the feeble zone, but this surrounds the pair of veins as a unit; if the veins were sufficiently close together, no sericite zone would exist between them, and alunite-dickite alteration would exclusively occupy that space. No actual example of this last-named case is known in the district.

It seems clear that the locus of the ore shoot was the "hot center" of the vein unit and that the lean pyritic end portions were cooler; also that the temperatures prevailing when and where the intense phase of rock alteration was developed were higher than those when and where the moderate and the feeble zones were formed. The zone boundaries may thus be looked upon as constituting also "temperature contours," the highest temperature being innermost and the lowest outermost. In this connection it is interesting to note that the mineral zoning and the "temperature contours" are not symmetrically disposed with respect to the length of the veins. The zonal distributions are such as to imply that the eastern portions of the veins and the adjacent wall rock were hotter than their corresponding western

portions. This may possibly be due in part to a little greater width of the veins toward their eastern than toward their western end, thus suggesting that solution flow and hence heat accession were somewhat easier on the east. But an additional and probably more adequate explanation is that the deposition of the enormous pyrite body on the east, which had (at least slightly) preceded the mineralization of the veins, had already heated up that vicinity so that the solutions ascending the eastern portions of the veins lost heat less rapidly and therefore built the temperatures higher than was true toward the western ends of the veins.

We have treated this matter of zoning in a somewhat detailed and elementary manner for a deliberate purpose. The conception that as the general mineralizing process went on, the several zones moved centrifugally from the central channelway, but each maintaining its own *relative* position to the others, makes sense from the standpoint of the chemistry, the temperatures, the textures and the sequences involved. Yet for such a region of mineral zoning there seems to lurk in the minds of some the notion that the innermost zone was formed first, that succeeding supply of solution moved through this zone with little effect upon it, and just outside formed the second or intermediate zone, and finally the last of the solution moved still farther out and formed the feeblest, peripheral zone. But that *doesn't* make sense; the plain facts of the chemistry, the textures and the sequences flatly contradict it. For purposes that follow, we desire to make most emphatic the fact that all the local evidence supports the conclusion that the innermost alteration zone, marked by alunite, dickite, zunyite, and quartz, is the *latest* of the zones, and that any logical consideration of the controls of mineral zoning will show that this innermost zone *must* be the latest zone and the minerals which constitute it are the last [9] of the new minerals to form.

[9] When stating the age of minerals in such an occurrence, it is essential to bear in mind that, on the basis of this progressive centrifugal displacement of zones, the "latest" mineral formed in the innermost zone may be actually no later in time than minerals of the middle or the outermost zone; for instance, deposition of, say, quartz at the inner edge of the intense zone may have been going on *at the same time* that chlorite was forming at the outermost limit of the feeble zone. Time designations, therefore, such as "early" and "late" cannot be applied usefully

NATURE OF THE SOLUTIONS.

Present Status of Opinion.

In the foregoing section, the object has been to record the pertinent facts that have been accumulated by many workers in the district. Attempt may next be made to relate and interpret these facts in terms of their probable genetic significance, and especially with respect to the chemical character of the solutions that deposited the ores and altered the rocks. As a first step, it may be well to record briefly the principal views now current as to the acid vs. alkaline character of solutions that deposit sulphide ores of the kind now commonly known as hydrothermal, *e.g.*, the hypothermal to epithermal ores of the Lindgren classification. It is now widely recognized that hot, ascending solutions of both characters actually occur and yield correspondingly diverse kinds of mineral product; but sharp difference of view exists as to their relative importance in ore genesis and related phenomena.

Those whose contact with the problem has been chiefly from the side of physics and chemistry lay great emphasis on the acid character of the fluids, and at the present time are generally unanimous in holding that the volatile emanations, as evolved from the magma, are or soon become dominantly acid. Thus Day, Allen, Zies, Fenner, and Bowen through numerous well-known writings are in various ways on record to this effect. Bowen has recently put the case thus:

> It is probably these acid solutions that are the principal agents of contact metamorphism, of vein formation, of replacement, and of metasomatism in general.[10]

These scientists explain the abundant evidence of alkaline reagent, whether manifested as alkaline hot springs at the surface, or as deeper rock alteration involving alkali addition, by the proposition that the early acid emanations become neutralized and eventually

over the zoned region as a whole but only with respect to a given unified part of the region, or else relatively as between one mineral and those closely surrounding it.

[10] Lindgren Volume, Ore Deposits Western States, Am. Inst. Min. Met. Eng., p. 123, 1933.

alkaline by selective leaching attack on the alkali-bearing minerals of the rocks through which the fluids pass. Fenner, vigorous supporter of the view that the volatile components leave the magma chiefly as gases of dominantly acid reaction, nevertheless recognizes the weight of observational evidence afforded by the ores and their immediate environs, and, as we read him, appears rather cautiously to agree with Lindgren (as quoted later) and others that the major job of *actual and known* ore deposition and adjacent rock alteration is accomplished by hot alkaline liquid solutions. After referring to the condensation of the gases to an aqueous solution, the progressive neutralization of the acids and the extraction of alkalies from the channel walls as a collective operation which he says "produces a solution of alkaline reaction," he adds:

> This is the sort of solution to which the formation of mineral veins as we see them is commonly ascribed, probably with good reason, but the principles developed and discussed on preceding pages render it doubtful whether these hydrothermal solutions ordinarily represent the first step in the extraction of ores from the magma.[11]

This hypothesis of the physicists and chemists that the fluids start out from the magma dominantly acid and later in their journey become alkaline by leaching of the rocks through which they pass has two very direct consequences of geological import. If that be the sequence of compositional character, then (1) wherever the action of alkaline solutions has gone on, there should exist below that locality (*i.e.* sourceward) a region of acid attack and alkali leaching; (2) wherever alkaline attack and acid attack occur in local proximity, the features resulting from the acid reagents should be the earlier and the minerals and textures produced by the alkaline solutions should follow later. Upon the degree of validity in these two propositions the facts at Cerro de Pasco fortunately throw very clear light, and will be further discussed shortly.

Most geologists have been led by their observations of the natural products to draw deductions different from those reached

[11] Idem, pp. 83–84.

by the chemists and physicists. In discussing this question in 1927, Lindgren said:

> The hot springs which the economic geologist has connected with ore deposits are . . . always alkaline. . . .[12]

In the latest edition of his "Mineral Deposits," he somewhat tempered this extreme statement, recognizing the development of hypogene kaolin and some other products by acid hydrothermal agents,[13] but he plainly still ascribed the major task of hypogene sulphide ore deposition and attendant rock alteration to alkaline solutions.[14] This emphasis on alkaline character appears to be pretty generally held by those whose chief experience with the problem has been gained from the essentially geological approach.

Bunsen[15] long ago proposed the formation of hot-spring sulphates through oxidation of other forms of sulphur by ferric minerals in the rocks. Much later, B. S. Butler, apparently accepting the view conventional among geologists that the usual hypogene sulphide ores have been deposited by alkaline solutions,[16] advocated a means similar to that of Bunsen whereby (sulphuric) acid can be developed in the solutions *after* these have departed an indefinite distance away from the magma source, namely, by the attack of sulphur or sulphur compounds on ferric compounds. In this way Butler contemplated the production of so high a concentration of sulphuric acid as would

[12] ECON. GEOL., vol. 22, p. 191, 1927.

[13] 4th ed., p. 457, 1933.

[14] Since the present paper was presented orally in New York, Lindgren has published an article (Succession of Minerals and Temperatures of Formation in Ore Deposits of Magmatic Affiliation, A. I. M. M. E., Tech. Pub. No. 713, 1936), in which his present position on this specific subject seems not as clear as before. For on pp. 6–8 he cites with apparent acceptance and approval the essentials of Bowen's mechanism that lead Bowen directly to the final conclusion that ores are formed by acid solutions. But after quoting this conclusion, Lindgren inserts a footnote saying "The writer cannot agree with Dr. Bowen when he says that most ore deposits are formed in depth through the agency of acid solutions."

[15] Liebig's Annalen, 62, 10, 1847; Ann. Chim. Phys., 38, 272, 1853—noted in Day and Allen: Volcanic activity and hot springs of Lassen Peak, p. 139, 1925.

[16] For in one of the districts which he evidently regards as best supporting his conclusions, Cactus, Utah, Butler shows sericite and quartz formed relatively much earlier than the hypogene sulphates. ECON. GEOL., vol. 14, p. 601, 1919.

attack potash-aluminum rocks and produce a mineral so rich in sulphate as alunite.[17] Although having before him the views of Ransome on formation of alunite at Goldfield by contemporaneous atmospheric oxidation of the mineral-forming solutions, Butler plainly concluded that alunite and other sulphates can form abundantly from solely hypogene solutions, that is, without any dependence whatever on surface-derived oxygen. In this last respect, he agreed with many other geologists, to a considerable number of whom he directly refers.

An alternative method of generating sulphuric acid in a previously alkaline liquid solution[18] of magmatic origin has been advocated by Graton, on the basis of some such reaction as that established quantitatively by E. T. Allen[19] from previously-known qualitative data, viz.,

$$4\ H_2O + 4S = 3H_2S + H_2SO_4.$$

Suggesting that such a scheme, of which the essential is that the oxygen comes from water, would satisfactorily explain the conversion of alkaline to acid solutions in ore deposits formed at no great depth, *e.g.*, the epithermal zone, Graton says:

> The consequences would be postulated as follows: If and wherever the proportion of (sulphuric) acid so produced in the solutions exceeds their natural inherent alkalinity, they will thenceforth fail to deposit carbonates and will attack any carbonate that may previously have been precipitated at or above the level where the change to acidity takes place. . . . Where the acid concentration becomes still stronger, definite attack will be made upon the alkaline silicates of the wall rock; in this way, the kaolin mineral, dickite, and, with still higher acid concentration, the sulphate-rich alunite, may result . . . the responsible acid is to be regarded wholly of hypogene

[17] *Op. cit.*, pp. 599 et seq.

[18] ECON. GEOL., vol. 28, p. 520, 1933.

[19] Personal communication, 1918. Allen's general result was also known to Butler, who refers to it approvingly on p. 604 of his paper on hypogene sulphates just cited, though evidently ascribing to it an importance subordinate to that which involves the reduction of ferric compounds. The same idea was adopted by Wandke (ECON. GEOL., vol. 20, pp. 314–315, 1925) to explain the formation of sulphuric acid for the hypogene development of alunite and hydrargillite. The reaction mentioned above was finally described by Allen, in Day and Allen: Volcanic Activity and Hot Springs of Lassen Peak. P. 139, 1925.

origin. That it resulted from atmospheric oxidation, as some have proposed, seems quite incompatible with the attendant geological facts. This extreme of acid development in the hydrothermal waters probably takes place only fairly close to the surface. There is even the possibility that it may be coincident with that occasional change of the solution from a dominantly liquid to a more or less gaseous state through rapid loss of pressure close to surface.[20]

From among the various and conflicting views cited in the foregoing selected summary of present-day opinion, can there be found an explanation that satisfactorily fits the conditions shown in the Cerro de Pasco veins? Let us attempt now an interpretation of the local facts recorded on previous pages.

Interpretation at Cerro de Pasco.

Alkaline Solutions Formed Moderate and Feeble Zones.

For reasons earlier indicated, the chemical nature of the changes that went on in the wall rock and the composition of the solutions that produced those changes and formed the attendant vein deposits may best be followed by consideration of what resulted in the quartz monzonite porphyry. The ensuing discussion will therefore be illustrated chiefly by allusion to effects in that rock.

The feeble and the moderate zones of rock alteration associated with the veins at Cerro de Pasco exhibit nothing particularly novel; their essential features can be duplicated in district after district where igneous rock of similarly intermediate composition has been acted on by solutions that formed sulphide ores neither too close to the surface nor too deep—say, ores of the leptothermal and mesothermal divisions.

There can hardly be challenge of the conclusion that solutions of alkaline character produced the alteration from the inner, most intense margin of the moderate (sericite) zone to the outermost limit of the feeble zone where alteration ceases and gives way to fresh rock. Working on rock which itself was of alkaline reaction, the solutions acting in these two zones could have no possible way of becoming acid if they were not already acid

[20] *Op. cit.*, pp. 541–542.

when they arrived. And that they were not acid then is demonstrated by the fact that throughout these two zones they have undoubtedly added alkali [21] to what was already present in the rock. This addition was surely greatest at the inner side of the sericite zone, where the solutions were richest in potash, and dwindled outward as their initial potash content became exhausted by sericite formation.

Acid Solutions Later Formed Intense Zone.

Emphasis has already been placed on the common presence in many regions of the calcite-chlorite-epidote zone and the sericite-quartz-pyrite zone associated in the same order. The combination can be regarded as a kind of double-barrelled unit. In most districts where this combination occurs, the inner of those zones is the most " intense " zone of rock alteration present, and comes right up against the most intense parts of the channelway deposits—right against the " hot center."

At Cerro de Pasco, however, the sericite-rich zone yields inward to the alunite-dickite-zunyite-quartz-pyrite zone, which has plainly attacked and more or less destroyed the sericite that earlier occupied the site. As already shown, this relatively narrow and somewhat erratic inner zone virtually sheathes the enargite ore shoots but does not continue far enough to envelop the lean pyritic portions that lie mainly toward the ends of the veins.

The texture and sequence leave no doubt that most if not all of the minerals characteristic of this innermost zone were formed by vigorous attack on the sericite. The character of these minerals indicates that this attack was acid, and the abundance of alunite plainly shows that the dominant acid was sulphuric. It is clear that there was a striking change in the nature of the

[21] It is probably not strictly true that alkali was added in those very outermost parts of the feeble zone where the only alteration minerals are chlorite, epidote and calcite. Such alteration represents the redeposition of the CaO and MgO that had been displaced farther inward by the conversion of plagioclase, biotite, apatite, etc., to sericite, and was accomplished out where the solutions had become incapable of still forming sericite. But even if this outermost fringe of the alteration does not represent alkali addition, there is certainly nothing about its character which suggests that the solutions responsible for it were acid.

solutions from those that deposited the abundant sericite to those that drastically attacked it and replaced it with these new combinations. The positional evidence, whether of the larger structural and zonal relationships or the minute features of texture, are permissive and presumptive of the close following of the alkaline solution by the acid. This is further strengthened by the gradational relations in the veins proper and the intimate relation of the enargite to the acid-formed alteration of the walls. It therefore seems probable, though this cannot now be proved, that *while the given body of solution was continuously flowing, it changed from strongly alkaline to strongly acid.*

It is to be recognized, however, that this zone of sericite displacement by the acid-formed minerals is a zone of alkali-subtraction; for alunite, although plentiful, is not abundant enough to incorporate all the potash of the sericite that was destroyed, nor abundant enough for its alkalies to equal the combined potash and soda present in the quartz-monzonite porphyry that originally occupied this site. It would therefore be possible, solely from the chemical standpoint, to entertain the idea that the solutions, as supplied through the channelways to the present explored region, were acid from start to finish. The sequence of events would then be imagined as follows, holding consideration as before to any given horizon of observation: The first of the solution to reach this horizon by ascent along the channelway would, if acid, attack the fresh porphyry of the immediate walls and produce alunite, dickite, etc., which we actually find. In suffering such replacing attack, the rock would yield alkalies, magnesium and calcium which, moving (in part) away from the vein, might attack the fresh rock there encountered, making first sericite, and, farther out, calcite, chlorite, etc. Thus would be formed the very start of the three zones we now see, in the same positional order. Continued flow of acid solution along the channelways would progressively widen each of these zones, with consequent outward encroachment of one upon another, until, with the eventual cessation of supply, the present distribution of the zones would exist.

This would be a very different genetic set-up from the one previously suggested. Three things, however, stand in the way of its acceptance:

(1) If the hot solutions started out from the source with an acid character (or if they became acid somewhere in their upward journey but below the horizon of observation) they would inevitably react with the alkaline rock of the walls, thus losing acidity and gaining alkalies. Only a relatively short distance of travel along the constricted fracture-ways would suffice to neutralize the very fore-front of the ascending column of solution and next render it alkaline. Therefore, unless the acid-yielding magma source (or the place where the solutions were rendered acid) were located only very shortly below the horizon of observation,[22] it would be inevitable that the very first of the solution reaching that horizon would be alkaline in character. Those who advocate the hypothesis of initial or early acidity of the solutions and their later conversion, by reaction with the wall rock, to alkaline condition appear to assume [23] that a solution when thus rendered alkaline can introduce alkali into its walls, *e.g.*, as sericite. This, however, appears to be a quite unjustifiable assumption provided the original wall rock is of equal alkalinity from top to bottom of the channelway system. At Cerro de Pasco there is no reason for thinking that wall rocks deeper than those known were richer in alkalies, but for the moment we may concur in the assumption mentioned while the consequences are being followed through. We may, therefore, imagine that the solutions that had become alkaline would deposit sericite close to the channelway and farther out deposit chlorite, epidote, etc. This would then duplicate the relations of the moderate and the feeble zones at Cerro de Pasco. In short, if one grants the (improbable) assumption mentioned, it would appear that at any place in alkaline rocks far enough from the source to have per-

[22] Every geological factor in the case indicates that the magma source does not lie shortly below the deepest Cerro level.

[23] *Cf.* Fenner, C. N.: Lindgren Volume, Ore Deposits Western States, Am. Inst. Min. Met. Eng., bottom of p. 83 to middle of p. 84, 1933; see also qualified acceptance by Allen, E. T.: Geyser basins and igneous emanations. ECON. GEOL., vol. 30, p. 9, 1935.

mitted alkalinization of the (supposedly) previously acid solution, the *early* alteration might be indistinguishable from that which would be formed by a solution alkaline from the beginning. But the fact that on first arrival at the horizon of observation the solutions were alkaline cannot fail to be at least a statistical tally against their having earlier been acid.

(2) If the solutions be assumed initially acid but capable of depositing alkalies when sufficiently alkalinized by contact with the rocks, then there should invariably exist some limiting quantitative relationship between the amount of alkali leached in the near-channel region of acid attack and the amount of alkali added in the region of alkaline attack lying next outside; in a word, the quantity of alkali added should never exceed and should ordinarily be less than the quantity of alkali leached. This should be true regardless of whether the forefront of the solutions be assumed to have reached the horizon of observation either in the initially acid condition or in a condition that had been rendered alkaline. As a matter of fact, the quantity of alkali added in the sericite zone at Cerro de Pasco very greatly exceeds the combined quantity removed in the inner zone, because the inner zone of acid attack is not only relatively thin and short about each vein but also it contains the alkali-rich alunite as one of its chief minerals. But if, as we believe, the solutions were first everywhere alkaline and produced the feeble and moderate zones first, the zone of acid attack need bear no fixed or limiting quantitative relation to the zone of alkali addition—it could be either important or insignificant. A relatively insignificant relationship is the actual case at Cerro. The quantitative factor is thus strongly against the idea that the solutions first to arrive were acid.

(3) If the first solutions to rise through the channelway at the horizon of observation were acid, then it would be expected that there would be in the channelways early precipitation of those sulphides which are found intimately associated with the regions of acid attack, namely, enargite, luzonite, and tennantite. As a matter of fact, these minerals are, on the whole, late min-

erals in the veins; they plainly follow most of the pyrite and in fact at places depended largely for their introduction on fracturing [24] that reopened the veins which had previously become plugged by pyrite. There is some pyrite associated with or slightly later than the copper-arsenic sulphides, but the quantity is greatly subordinate to the pre-arsenic pyrite. If the acid solutions ascended first, moreover, they should have had opportunity to precipitate their copper-arsenic sulphides through the full (horizontal) length of the channelways, and should likewise have produced acid attack on the walls from end to end of the channelways. The fact is, however, that the copper shoots are restricted and so are the enveloping sheaths of acid-altered rock, while endwards occur only lean pyrite and associated sericite alteration, both of earlier formation.

Thus, on all three scores the postulate that the solutions along the fracture channelways were initially acid breaks down and must be abandoned. The only alternative is that the first solutions to reach these levels were alkaline, and in fact that idea fits the facts as well as the opposite idea fails to fit them. This does not prove that the solutions *at the magma source* were also alkaline (though we believe this to have been the case), but it does indicate that, rather late in the total period of solution activity, after a great quantity of alkali addition had been accomplished, the solutions moving through the channels at the known levels underwent a change from strongly alkaline to strongly acid.

Cause of Change from Alkaline to Acid.

Plainly enough, the change in character from alkaline to acid cannot be ascribed to any acidifying effect of the wall rock—not even if very different kind of rock were imagined to exist deeper down the channelways, since practically all rocks impart an alkaline reaction to hot water. It is therefore necessary to look to some change in composition, either in the solution as supplied at the source, or else within the solution somewhere in the course

[24] This has been made especially clear by the studies of O. C. Schmedeman directly upon that question.

of its ascent. If the early solutions leaving the source were alkaline, there is no evident reason why the later solutions should depart in acid condition. If there *is* an important stage of acid emission from a magma it should come early rather than late in the cycle of liberation of volatiles. Therefore, the indicated change in composition of the solutions apparently must be accomplished by reaction within the solutions themselves.

A clue to such reaction is immediately suggested by the fact shown by the abundant alunite that the acid dominantly responsible for the alteration of the intense zone was sulphuric acid, not a halogen acid. Now sulphuric acid can liberate the halogen acids from their salts, but the halogen acids cannot liberate sulphuric acid from sulphates. Therefore, the acid condition must have been due from its very inception to sulphuric, not halogen, acid. This, in itself, is a serious handicap to the view that the emanations left the magma in the acid condition and in the gas phase. But the abundance of sulphides which practically all hydrothermal deposits carry shows that sulphur was lavishly available in the solutions from their beginning. Therefore, all that is needed is a means for converting some of the sulphur into sulphuric acid. As will appear, opportunity probably existed for such conversion.

Butler's survey of the hypogene sulphates has clearly shown that they are scanty or wanting in the ores of deep-seated character; their characteristic home is in positions where the cover was not excessive. Barite, the most insoluble of the sulphates, apparently can form even in alkaline solution, as soon as any SO_3 is formed to combine with the BaO.[25] But because of its intimate association with dickite, it seems safe to assume that alunite does not form until enough H_2SO_4 has been formed to remove completely the initial alkaline character of the solution and build up a considerable acidity; and alunite appears, on the whole, to have a shallower-seated bottom limit than does barite.

Three independent ways of generating H_2SO_4 in the solutions have been advanced. They all depend upon oxidation of sulphur

[25] Perhaps in less degree the same is true for anhydrite.

or of some sulphur compound. Ransome's [26] final proposal of oxidation at the surface and downward flow while the general upward mineralization was in progress, highly improbable even for Goldfield for which it was invented, may be at once dismissed as entirely inapplicable to Cerro de Pasco. Not only do alunite and dickite occur intensively far below any other indication of supergene action, but their close positional and selective relationship to the copper-arsenic ore shoots (which are unquestionably hypogene) and their intergrowth with clear, crystalline epidote, clearly testify that these acid-formed minerals are hypogene also. The only fact that could possibly favor the supergene origin of alunite and dickite is the tentative indication that they may be somewhat less plentiful on the lowest level than elsewhere above; but this if confirmed would be equally well explained by the plausible assumption that the 2100 level (which was then perhaps 5000 feet or more below the volcanic surface) is reasonably near the still deeper place where generation of H_2SO_4 became sufficient to start the formation of alunite and dickite.

The other two proposals for generating sulphuric acid depend on non-atmospheric oxygen. The oxidation of sulphur or sulphur compounds by ferric minerals, first proposed by Bunsen and later elaborated by Butler, does not seem well applicable to the facts at Cerro. The quartz-monzonite porphyry and other rocks of the district carried too little magnetite to explain the quantity of H_2SO_4 that must have been involved. No ferric minerals are known in the ores except epidote, which intergrows with the alunite and dickite and is thus evidently stable toward them; and there is no indication that other ferric minerals have been destroyed. As has elsewhere been said in this general connection: "To accomplish this (*i.e.*, hypogene generation of H_2SO_4 and formation of alunite and dickite), a means probably more competent and more restricted to this definitely shallow region would be required than the interesting proposal by B. S. Butler." [27]

The hypothesis of sulphuric acid generation by reaction of a

[26] Ransome, F. L.: Geology and Ore Deposits of Goldfield, Nevada. U. S. Geol. Surv., Prof. Paper 66, pp. 193–195, 1909.

[27] Econ. Geol., vol. 28, p. 541, 1933.

sulphur-bearing compound with water seems to us satisfactorily to fit all the facts regarding alunite, dickite, etc., at Cerro de Pasco, even though those facts were not known and the mine was only half as deep when the hypothesis was developed. The Cerro occurrence therefore affords effective support to that general hypothesis. It shows, however, that in one respect Graton's statement of this hypothesis must be modified at least for this particular example; for instead of the sequence being invariably first dickite and then, with further attack of acid, alunite, as he supposed, the two are often essentially contemporaneous at Cerro, and still more commonly alunite was slightly the earlier, so that there are pseudomorphs of dickite after alunite. It would appear that the determining factors of equilibrium were more complex than the simple concentration of H_2SO_4 as supposed by him. Interesting light on this situation is afforded by the following tabulation of compositions of the three minerals most intimately involved in the acid attack:

Mineral.	Composition.				
	SiO_2.	Al_2O_3.	K_2O.	H_2O.	SO_3.
Sericite	45.2	38.5	11.8	4.5	—
Alunite	—	37.0	11.4	13.0	38.6
Dickite	46.5	39.5	—	14.0	—

The most striking feature is that, under the dominant control of the alumina, the most difficultly transportable of the several components, it is a toss-up whether alunite or dickite shall develop from the sericite; as a secondary control, it seems to be a question whether the silica shall remain essentially constant and the potash and water change, thus giving dickite; or whether the potash shall hold, water change and SO_3 take the place of SiO_2, thus giving alunite. The similarity of alunite and dickite in alumina and water is also noteworthy in view of the indicated delicate balance between these two minerals in the altered rocks.

Locus and Conditions of Acid Generation.

The geological evidence is overwhelming that most ores of the hydrothermal family, regardless of depth, are associated with alkaline attack on their walls. The data assembled by Butler show that the hypogene sulphates are relatively shallow-seated rather than deep-seated minerals; and the same appears true for dickite and other hypogene kaolin minerals. These facts combined make it seem altogether probable that the H_2SO_4, which causes the solutions to be acid and which produces the alunite, dickite, etc., is generated in the solutions preferably at relatively shallow depths.

Presumably a sounder way of stating the situation would be that when the pressure is too great, H_2SO_4 apparently does not form in abundance. However, when, under not too great pressure, there is plentiful sulphur (in one form or another) and not too low a temperature, the sulphur and water may react in the oxidizing way indicated by Allen's reaction already quoted. He found that reaction to operate in a closed tube "at 250° and possibly as low as 200° C."[28] Such temperatures would be altogether likely in the upper part of the hydrothermal range; and would imply a pressure of not more than 35 atmospheres, which certainly could occur only at relatively shallow depth. Inasmuch as a high-volatile compound, H_2S, is a product of Allen's reaction, it may well be that, at the same range of temperatures, high pressure would retard or inhibit the reaction. That the production of free H_2SO_4 is negligible or entirely absent in most shallow-seated hydrothermal deposits, where a temperature range of 200°–250° C. is probable, is shown by the general absence of alunite and hypogene kaolin minerals. Therefore, there would seem to be some justification for the view that free H_2SO_4 and these mineral products of it form on an appreciable scale only where, in relation to the temperature, the pressure is abnormally low. Such a situation would appear beautifully to fit the case at Cerro.

[28] Day and Allen: Lassen Peak. *Op. cit.*, p. 139. The rate of reaction is said to be negligible at 100° C.

Let this question be examined further in the light of the temperature-pressure balance. In the typical average channelway utilized for vein formation it appears, from such indications as we can deduce, that as the solution ascends, its temperature and pressure fall off in a relatively characteristic ratio to one another. That is to say, the rate of loss of temperature to loss of pressure varies within some given range of limits for channelway after channelway. Furthermore, in what may perhaps be regarded as the normal case, there is a tendency to maintain about this same rate of temperature change to pressure change with time as the mineralizing process goes on. Continued flow of hot solution heats up the walls faster than conduction can keep their temperature down, thus the solution moving through the channelway loses heat more slowly than before and hence the later solution passing any given level is hotter than its earlier counterpart at that place.[20] But in the meantime, deposition of solutes from the solution has probably been tending to plug up the channelway and thus to increase the pressure on the solution; in this way the original relative balance between pressure and temperature tends to be maintained.

However, at depths of a few thousand feet (*i.e.*, relatively shallow by the standard of the whole hydrothermal range), either of two things can cause an upset in this "normal" relation of temperature to pressure:

(1) If the rocks through which the channelway passes do not have the temperatures normal for their depth according to the geothermal gradient appropriate for the general locality, but have, instead, been *pre-heated* by the shortly prior effects of near-by intrusion or effusion, then the solutions passing up along the channelways would lose heat less rapidly than normal, and so would reach any given distance below the surface at an abnormally high temperature. But the fractures in such pre-heated rock would probably be just as free and open (indeed, perhaps more so) than in non-pre-heated rock at corresponding depth;

[20] That is to say, mineralization ordinarily proceeds on an ascending temperature scale, not a descending one as so often assumed. See ECON. GEOL., vol. 28, p. 521, 1933.

therefore the rate of pressure loss as the solutions ascended would probably be as rapid as normal.

(2) If under "normal" temperature conditions, *i.e.*, rising temperature as flow of the hot solution continues, structural accidents occur to fracture (reopen) the deposit already formed and free up the passageway, the pressure on the solution will tend to drop while the influence on temperature will remain substantially as before.

Both of these causes thus operate in the same direction: to keep the temperature high in terms of pressure. If both these causes should operate conjointly, that is, if pre-heated channelways should be reopened by sudden fracturing while the solution was still flowing, there would be a double tendency to reduce pressure in relation to temperature.

It is the belief of the writers that the "normal" relation between change of temperature and change of pressure in the usual hydrothermal vein is such that the fluid is maintained chiefly if not wholly in the liquid state; that is to say, temperature falls fast enough in relation to the fall in pressure toward the surface so that the tendency of the solution to boil is never carried into action to a dominating degree. But where temperature is maintained to an abnormal degree in relation to pressure—as by preheating—or where pressure abruptly drops in relation to temperature—as by reopening—then, if either of these tendencies is sufficiently great, the previous liquid may boil in corresponding degree, the more volatile components responding first and the less volatile ones tending to remain liquid. Moreover, whether or not any boiling in the simple sense may go on, any possible reactions in the solution which would be favored by relative reduction of pressure to temperature would tend to take place. The Allen reaction, with its production of H_2S, is such a reaction; H_2SO_4 is its other product.

The situation at Cerro de Pasco seems built to order as an illustration of these consequences. The veins are formed in and close to a volcanic explosion vent of large dimensions which must have been immediately filled with its own explosion debris—hot?

It was next invaded by bodies of (hot) quartz-monzonite porphyry. Quickly afterward followed the mineralization process. The chance for some pre-heating is excellent. Then, after the filling of the veins, chiefly by pyrite, had been practically completed, and the sericite and the chlorite-calcite alteration zones produced, marked fracturing and sheeting took place right down the middle of the widest parts of the larger pyrite veins. It is adjacent to these reopened portions of the pyrite veins that the acid attack has converted the prior sericite into alunite, dickite, zunyite, and late quartz. It is in these fractured portions of the pyrite veins that the late deposition of copper-arsenic minerals has produced the ore shoots.

Little emphasis has thus far been put on the special kind of silica that intimately accompanies the alunite and dickite, especially very close in against the ore-bearing portions of the veins. The reason is as follows: although such silica has visible characteristics of grain-size, turbidity, inclusions, etc. which serve generally to permit its distinction from the quartz that accompanies sericitization, its composition carries no proof (as does that of alunite and of dickite) that it was in fact a product of *acid* solutions; and inasmuch as clarity demanded that the surely acid-formed minerals be emphasized, this accompanying quartz has not hitherto been brought into prominence. However, if it is fair to regard alunite, dickite, zunyite, etc. as belonging to the inner, intense zone, then it is equally fair to regard this silica as the *most* intense and innermost of the rock alteration minerals associated with the veins. That it was, like them, a product of acid solutions seems altogether probable.

In connection with this silica there is a feature of possibly considerable significance. The great pyrite replacement body, which lies along the eastern boundary of the filled vent, plainly preceded the formation of the veins, for some of these continue eastward directly into and even across the pyrite; there is no doubt that the vein fractures and the vein filling are later than the pyrite of the great body. The introduction of this enormous, concentrated

tonnage[30] of pyrite by hot solutions had almost certainly been attended by a marked heating up of its immediate surroundings. It is reasonable to suppose that this local heating had not been dissipated when the veins were formed. Now the point of special interest is that the relationship of alkaline to acid attack is not distributed identically and symmetrically at the two ends of the veins. The east ends, near the pyrite body, tend to show possibly greater amounts of alunite and dickite in proportion to sericite, and surely greater quantities of this late silica than do the west ends of the veins. On the whole, there is more and better copper-arsenic ore in the eastern half of the veins than in the western half away from the great pyrite body. In short, the intensity of acid attack seems emphasized near this pyrite mass. On the hypothesis already mentioned that pre-heating would favor the generation of acid, this state of affairs appears suggestive, to say the least.

It is impossible to decide from the local evidence whether or not boiling, in the simple sense of change from liquid to vapor with rising temperature, actually took place as deep below the surface as the levels now opened in the mine; but the tendency toward boiling must have increased by fracturing within the veins, and certainly a reaction yielding a gas (H_2S),[31] would be favored, presumably to an extent adequate to account for the amount of attack by sulphuric acid actually seen.

Vertical Range.

The occurrence on the 2,100-foot level at Cerro de Pasco appears to be one of the deepest, if not indeed the very deepest, at which important hypogene alunite has been noted.[31a] Presumably the same is true for hypogene kaolin—in this instance dickite. These minerals are usually thought of in especial association with epithermal ores. At Cerro de Pasco, the veins apparently belong

[30] The portion of this body lying between the present erosion surface and the 2,100 level contains something of the order of 500,000,000 to 1,000,000,000 tons.

[31] It is to be noted that *any* variant of the Allen reaction as given, which would still derive the oxygen (or part of it) for H_2SO_4 from water, would yield H_2S as a product.

[31a] See footnote on page 698.

in the upper mesothermal division, perhaps just overlapping into the lower part of the leptothermal. It may thus be entertained on both counts that the alunite, dickite, etc., found on the lowest 2,100-foot level at Cerro are pretty well toward the bottom of the range within which those minerals are formed. We are thus led to speculate as to the depth to which the effects of acid persist below the present bottom-most level. If the acid be deemed to have come as such all the way or nearly all the way from the magma, as postulated by Day, Allen, Bowen, and Fenner, then acid attack should persist down to unknown distances below the present mine-bottom, the region affected by such attack should enlarge in cross-section downward, and the qualitive intensity of the acid attack should increase toward the source. On the other hand, if the acid has been generated at such relatively moderate depth below the surface that the pressure there acting was low enough to permit an expansion type of reaction which would produce H_2SO_4 as a product, then there should be at such depth a (transitional) bottom of the region attacked by acid, and the cross-section of such attacked region should increase upward to whatever extent the condition favoring the reaction was intensified by lower pressure acting at higher levels. If the generation of acid did not start too late in the general episode of hydrothermal ascent and was continued long enough, the region of acid attack would continue through all the way to the surface.

In which of these categories does the Cerro occurrence seem to fit? As a matter of fact, although the presence of alunite as one of the alteration minerals of the district has been known for several years, it is only recently that its scheme of distribution with respect to the veins has been recognized; the same is true of the dickite, identified only recently as an accompaniment of the alunite. Reliable quantitative data on the distribution of these minerals are not yet available sufficiently to permit secure generalizations to be drawn. At present, one can do no more than form general estimates of quantities based on his best judgment from such inspection and restricted sampling as has been done. This much at least can be said: there is certainly no increase in

the proportions of alunite and dickite on the 2,100 level as contrasted with what has been found on higher levels. On the contrary, there are indications that although the widths of the alunite-dickite margins of the veins average about as wide on that level as above, the quantity of those minerals per unit volume of rock is somewhat less than it is above—that is, the intensity of acid attack is perhaps showing signs of tapering off with depth. It is hoped that continuing investigations by the local staff may in time yield definite quantitative data on the relative distribution of the acid-formed minerals and on their abundance relative to one another with depth.

So far as the available indications permit judgment, therefore, the facts of occurrence seem to favor the view that the acid was generated in and somewhat below the region of present observation rather than that it came all the way through from the probably deeper region where the main body of magma crystallized.

Taken as a whole, the evidence at Cerro de Pasco strongly favors the view that the ore forming fluids were originally and for a long time alkaline and liquid; but that at no excessive depth below the then-existing surface, and probably not very far below the present bottom level, the solutions at a rather late stage in the entire process became acid through the local generation of H_2SO_4 and thus from there upward superimposed close to the channelways an acid attack on the prior larger region of alkaline attack. Whether or not boiling attended this generation of acid and emphasized the degree of acidity attained (by excluding alkalies from the vaporized phase) cannot be decided; but the quantity of acid evidently formed, the openness of the channelways along which the acid attack is associated, and the reasonable proximity of the known horizons to the surface existing at the time of mineral formation would seem to encourage the guess that the phenomenon of boiling did accompany the generation of the acid.

One may now try to visualize what was happening at the surface as it then existed. It is hardly to be doubted that the fluids

were escaping at the surface. At the outlets of those channelways which had felt less pre-heating, or in which some constriction at depth had slowed the rate and quantity of flow so that the solution had not so markedly heated up its walls and thus itself emerged at a lower temperature, or to which perhaps, relatively close to the surface, there had been cooling accessions of groundwater—at such outlets there would be a flowing hot spring, alkaline in composition at the orifice as at the source and attended by adjacent rock alteration of an appropriate alkaline character because of the alkali content brought all the way from the magma. These channelways would correspond to the veins which, in the mine, carry mainly barren pyrite.

On the other hand, at the outlets of those channelways which were particularly affected by pre-heating (as by local dikes, the great pyrite body, etc.), or along which there had been greatest heating of the walls by the moving solution, or an effective reopening to cause lowered pressure in the upper reaches all the way to the surface—along such channelways there could be more or less boiling and at their outlets steam would issue in corresponding volumes. If the escape was mainly or wholly as steam, this would tend to be acid in composition through leaving behind the less volatile alkaline components, and the neighborhood of the orifice would thus show acid attack. Deeper down, some of these channelways would be the ones which in the mine carry the enargite ore shoots. Although development of sulphuric acid had been the initial cause of the acidity, little or no free sulphuric acid might reach the surface; a large part of it had reacted somewhat farther down to form alunite, which precipitated near the channelways. But any halogen compounds present in the solution or existing in the rock (as in apatite, biotite, etc.) would be converted into halogen acid when the H_2SO_4 was generated in the solution, and, save for the small quantity of halogen elements fixed in zunyite, could come *as acid* through to the surface. The same would be true for other acids weaker than sulphuric (such as boric, carbonic, etc.). The presence of halogen acids and other acids in the surface fumaroles, would therefore be no proof

whatever that these had existed as such all the way through from the magma source.

Intermediate between the alkaline springs and the acid fumaroles there might be outlets which would yield intermittently and alternately liquid and gas, possibly thus giving the geyser mechanism. Where the weight of liquid would much exceed the weight evolved as gas, as would probably be true for most geysers, the general composition would still be alkaline.

Thus might conceivably be developed in relatively close proximity to the surface the causes of the contrasting phenomena of present-day hot spring regions.

Metallogenetic Significance.

The indicated conversion of the later portions of the ascending alkaline solutions into an acid condition through the generation of sulphuric acid appears to have been attended by a reduction of solubility of copper and arsenic previously carried easily while the solutions were alkaline. Thus were formed, by a kind of hasty dumping or "telescoping," the copper ore shoots of the veins in very intimate relation to the sheaths of acid-altered wall rock. Just where along the change upward from maximum alkalinity to maximum acidity this precipitation of enargite, luzonite and tennantite started is not clearly revealed by present mine developments; therefore it is impossible as yet to predict as to the general depth to which these minerals will persist. Neither is it now known whether, where and if these minerals do eventually play out, they will be succeeded downward by copper deposition in the form of chalcopyrite, as seems to be the case below certain of the great enargite shoots of Butte and indicated also at Morococha.

The notable association of the ore shoots with loci of lengthwise fracturing of the preceding heavy pyrite that first filled the veins, and the tendency of the veins to be of somewhat better grade near the place of probably localized heating by the main pyrite body, emphasize the presumptive importance of high tem-

perature in relation to pressure, and thus of pre-heating and re-opening for the formation of the ores.

Although there are obvious dangers in stretching generalizations too widely from a single occurrence, the idea suggests itself that enargite, luzonite, and famatinite may, as a rule, be formed from solutions of either low alkalinity or outright acidity. In the main, these minerals appear to occur without carbonate as a gangue or near-by alteration mineral, and when occurring in limestone, as at Tintic, they seem to be kept away from the fresh rock through the intervention of a silicified envelope or sheath. In a number of districts one or more of these copper-arsenic sulphides is associated with hypogene sulphates, as follows: Cerro de Pasco, alunite; Morococha, anhydrite and gypsum; Goldfield, alunite; Tintic, barite and alunite; Butte, barite and alunite [32]; Bor, Serbia, barite; Chuquicamata,[33] barite and (possibly hypogene) alunite. At Butte, Kennecott, Cerro de Pasco, Chuquicamata,[33] and Bor these copper-arsenic sulphides are associated with covellite which in at least the first three districts, and possibly in all, is hypogene. Covellite is a sulphide which, to judge by its behavior under supergene conditions, has such a considerable stability toward H_2SO_4 that it can form in a higher acid concentration than is usual for the enrichment zone.

RÉSUMÉ.

In the Cerro de Pasco district, pyritic veins carrying enargite ore shoots occupy fractures in and close to a great breccia-filled explosion vent. The wall rocks show a zonal alteration embracing an outermost feeble chlorite-calcite-epidote zone, an intermediate sericite-quartz-pyrite zone, and an innermost, intense zone characterized by alunite, dickite, zunyite, quartz, and pyrite. This last-named zone forms narrow and somewhat erratic sheaths for the veins where these carry copper-arsenic ores; but the lean pyritic parts of the veins are contained in the sericite zone. The

[32] Recently identified by J. A. Noble and O. C. Schmedeman.

[33] Berkey, C. P., and Kerr, P. F.: Private Report quoted by Taylor, A. V., Jr. Copper Resources of the World, 16th Intern. Geol. Cong., vol. 2, p. 480, 1935.

two outer zones are plainly due to alkaline solutions, and the innermost zone to acid solutions, H_2SO_4 clearly being the principal acid involved. The broader relationships as well as convincing textural evidence show that the acid solutions followed the alkaline and superimposed their effects on the previously-formed sericite zone.

It is concluded that the solutions were at the start everywhere alkaline; but that relatively late in the period of mineralization and in the upper reaches of the channelways, sulphuric acid was generated in the solutions by the oxidizing reaction of water on some form of sulphur which the alkaline solutions had carried abundantly. The nature of this reaction is such that it would be favored by a low ratio of pressure to temperature, and such a ratio would be especially likely if pre-heating of the channelways and reopening by fracturing of the earlier-formed pyrite veins had occurred. Both pre-heating and reopening probably happened at Cerro de Pasco; and the ore shoots, with their sheaths of acid attack, are rather notably located where there has been longitudinal fracturing of the earlier pyrite veins. The possibility of pre-heating near and by the great pyrite body is linked with somewhat better ore in the veins in that vicinity. The ore shoots are thought to be due to the fact that copper and arsenic, which the alkaline solutions had been able to carry, lost solubility where and when the solutions became acid by H_2SO_4 generation, and were thus dumped rather abruptly.

The idea is proffered that enargite, luzonite, and famatinite may deposit preferably from solutions of low alkalinity or actual acidity; and the association of hypogene covellite and sulphates with enargite in several districts is cited as suggestive of such condition.

The conception is ventured that the varied manifestations of modern hot spring regions may well have been represented at the surface above where the Cerro veins were forming, and that all these phenomena might result from initially alkaline liquids that in places later became acid and possibly gaseous at no great depth.

The relations of time and position between the alkaline and

the acid solutions and their work, revealed with unusual clarity at Cerro de Pasco, have deep implications as to the origin of hypogene sulphide ores. The local facts are interpreted as rationally explaining the development of acid solutions without assuming that the emanations when departing from the magma were acid and gaseous. Instead, alkaline liquid emanations appear to be favored.

LABORATORY OF MINING GEOLOGY,
HARVARD UNIVERSITY,
July 2, 1936.

[31a] (Footnote from page 691.) Perhaps an equally deep or slightly deeper occurrence of alunite is that described by Lindgren and Creveling at Potosi, Bolivia (ECON. GEOL., vol. 23, pp. 242, 244, 1928); it is not entirely clear whether they found alunite throughout the developed range of 750 meters.

SOME PHYSICAL PROPERTIES OF CERTAIN IRON OXIDES.[1]

W. H. NEWHOUSE AND J. P. GLASS.

In this paper an oxidation product of magnetite is partially described; as determined by polished section study and x-ray diffraction patterns. Chemical analyses of mixtures of this mineral and magnetite are given. The mineral corresponds in properties to the unanalyzed and imperfectly described mineral maghemite, of Wagner and Schneiderhohn. Some of the magnetic properties of powders of these mixtures, and of ordinary magnetite are given.

The results should be of interest to those engaged in the study of many iron ores, and to the geophysicist dealing with ferromagnetism in the earth's crust.

COMPARISON OF CERTAIN IRON OXIDES.

Artificial ferromagnetic ferric oxide, with a cubic lattice similar to magnetite, has been known for some time to laboratory workers.[2] It may be produced in several ways, one of which is by oxidizing magnetite, another by dehydrating lepidocrocite

[1] The magnetite which has been described as relatively brownish compared to adjacent magnetite is regarded in *some* cases as a polishing phenomenon developed in certain magnetites that are generally of low titanium content. It is not certain that it is all the same. Some of it may be a surface phenomenon developed by polishing, but part of it appears to be unrelated to the polishing method used, and may be dependent on original differences in the magnetite. Its exact nature is unknown and it is not considered in this paper. Alling, H. L.: Geology of the Ausable Quadrangle (N. Y.). New York State Museum, Bull. 261, pp. 113–114, 1925. Newhouse, W. H., and Callahan, W. H.: Two kinds of magnetite? Econ. Geol., vol. 22, pp. 629–632, 1927. Newhouse, W. H.: The identity and genesis of lodestone magnetite. Econ. Geol., vol. 24, pp. 62–67, 1929. Hickok, W. O.: The iron ore deposits at Cornwall, Pennsylvania. Econ. Geol., vol. 28, pp. 218–223, 1933.

[2] For early literature see: Sosman, R. B., and Posnjak, E.: Ferromagnetic ferric oxide, artificial and natural. Jour. Wash. Acad. Sci., vol. 15, pp. 329–342, 1925. Twenhofel, L. H.: Changes in the oxidation of iron in magnetite. Econ. Geol., vol. 22, pp. 180–188, 1927.

($Fe_2O_3 \cdot H_2O$). Some recent work by Williams and Thewlis[3] showed that 4.40 per cent. water was present in ferromagnetic Fe_2O_3 formed by dehydrating lepidocrocite, this amount of water still remaining on heating to 300° C.

The presence of 4.15 per cent. water in artificial ferromagnetic ferric oxide had been previously described by Frebold and Hesemann.[4]

These and similar ferromagnetic compounds have recently been reviewed from the structural chemistry viewpoint by Bernal and Crowfoot.[5]

Some years ago Wagner[6] proposed the name maghemite for a "magnetic ferric-oxide" which occurred in intimate intergrowth with ilmenite that was found in the upper Norite zone in the Bushveld Igneous complex. It was considered to have been formed by weathering of magnetite. No evidence was given to show that the maghemite did not not contain the titanium that would be expected in such an occurrence.

Later Schneiderhöhn gave a microscopic description of the maghemite[7] from the original locality, and mentions it as occurring in titaniferous magnetite from the Katzenbuchel and elsewhere.

Then Walker published an analysis of material collected from the Norite zone of the Bushveld complex at Bon Accord, Transvaal.[8] This lodestone contained SiO_2–.50, TiO_2–15.50, Al_2O_3–1.42, Fe_2O_3–63.76, FeO–16.43, MgO–1.12, MnO–.37, H_2O–1.34. It was described as having the following properties:

[3] Williams, R. D., and Thewlis, J.: The heat treatment of the monohydrate of ferric oxide. Trans. Faraday Soc., vol. 27, pp. 767–771, 1931.

[4] Frebold, G., and Hesemann, J.: Über magnetischen und nichtmagnetischen Eisenglanz und seine Bedeutung für die Erzlagerstattenkunde. Centr. für Min., p. 315, 1926.

[5] Bernal, J. D., and Crowfoot, D. M.: Crystallography ann. repts. Chem. Soc., vol. 30, pp. 401–404, 1934.

[6] Wagner, P. A.: Changes in the oxidation of iron in magnetite. Econ. Geol., vol. 22, pp. 845–846, 1927.

[7] Schneiderhöhn, H.: Neues Jahrb. Referate, pp. 368–369, 1928. Ibid, Lehrbuch der Erzmikroskopie, Band 2, pp. 535–537, 1931.

[8] Walker, T. L.: Lodestone from Bon Accord, Transvaal. Univ. Toronto Studies, Geol. Ser. No. 29, pp. 17–19, 1930.

95 per cent of the material is a single anisotropic mineral as determined in polished section; a small amount of limonite is present, and the very fine powder is black with a faint chocolate tint. No x-ray or complete polished section description was given. On dissolving the mineral, the titanium, if present as Ti_2O_3, would reduce the iron according to the following equation

$$Fe_2O_3 + Ti_2O_3 = 2\ FeO + 2\ TiO_2.$$

This interpretation by Walker would indicate that only 2.48 per cent FeO was present in the mineral, and he suggests that the formula of the dominant mineral is $(FeTi)_2O_3$. He concludes: "This investigation seems to indicate the need of a mineral name for the magnetic oxide $(FeTi)_2O_3$ and the writer suggests that the name maghemite be reserved for this combination rather than for ferromagnetic ferric oxide as originally suggested by Wagner."

A comparison was made in polished sections and by x-ray diffraction patterns, of the material used in the present study with the original ferromagnetic ferric oxide from a gossan at Iron Mountain, Shasta County, California, described by Sosman and

TABLE I.

CHEMICAL ANALYSES OF IRON OXIDES.

Minerals and Locality	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	TiO_2	Total
Magnetite								
(1) Lovers Pit, Mineville, N. Y.....	0.27	0.21	68.85	30.78	Tr.	Tr.	Slight tr.	100.11
Magnetite and maghemite								
(3) Windpass Mine, B. C.....	0.53	Tr.	75.26	24.48	0.10	Tr.	Tr.	100.37
Magnetite (Titaniferous magnesioferrite)								
(4) Siberia.....	1.22	6.72	52.54	26.71	6.65	0.09	5.70	99.63
Magnetite (Titaniferous magnesioferrite)								
(5) Norway.....	0.14	5.64	54.97	26.69	5.15	0.10	7.57	100.26
Magnetite (Titaniferous magnesioferrite)								
(6) Magnet Cove, Ark...	0.13	15.14	46.95	26.58	5.83	0.11	5.01	99.75
Maghemite and magnetite								
(7) Alameda Co., Calif...	1.15	0.04	89.15	8.67	Tr.	Tr.	1.37	100.38

MARY G. KEYES, Analyst.

Special care was taken in determining the Fe_2O_3 and the FeO. The above figures on these oxides represent the mean of two separate determinations in close agreement. The numbers given under heading "Minerals and Locality" refer to the numbers on curves, Figs. 2, 3.

TABLE 2.

PROPERTIES OF SOME IRON OXIDES.

Mineral and Locality	Form of Mineral	Composition	Color of Powder	Ridgway Color No. of Powder	Hardness in Polished Section	Color in Polished Section	Optical Character	Space Lattice	Authority
Artificial ferromagnetic ferric oxide	Powder	Fe_2O_3 (a) Over 4% H_2O present in some.	Hessian brown to Liver brown; also bay.	6′ m 7 m	?	?	?	Isometric like magnetite	Sosman & Posnjak Ref. 2 (a) Williams & Thewlis Ref. 3
Natural ferromagnetic ferric oxide, Iron Mountain, Shasta Co., Cal.	Powder * Many particles show colloform banding in polished section	Fe_2O_3 plus 3.1% H_2O at red heat; also 2.4% FeO	Coarse powder burnt Umber. Fine powder Hazel	9″ m 11′ K	* Polish hardness less than Bon Accord maghemite. and nearly same as Mineville magnetite	* Gray, may show internal reflections	Isotropic in general. Some anisotropic. * In polished section isotropic	Isometric like magnetite. Cell edge a_0 8.30	Sosman & Posnjak Ref. 2 N. W. Buerger * Newhouse Data obtained from polished briquettes
Maghemite Upper part of Norite Zone Bushveld Complex, S. A. (Type locality)	In intimate intergrowth with ilmenite, which occurs as grains and minute oriented lamellae	Said to be Fe_2O_3 but no proof of absence of Ti. Complete analysis not made	Brown	?	Greater than magnetite, less than hematite	White to gray blue. With oil immersion gray, like hematite	Isotropic	Isometric like magnetite	Wagner & Schneiderhohn Refs. 6 & 7
Maghemite Norite Zone Bushveld Complex, Bon Accord, Transvaal, S. A.	Maghemite * Replacing magnetite which remains as small residual masses, in intergrowth with ilmenite. A little limonite present. Fine grained	Aggregate consisting largely of maghemite contains 15.5% TiO_2. * Microchemical tests show Ti in maghemite	* Fine powder near bone brown		* Greater than magnetite, less than hematite. Hardness in briquettes same as maghemite from Alameda, Cal.	* White to gray blue. With oil immersion gray, like hematite	* Isotropic	Isometric like magnetite. Cell edge a_0 8.31₉	Walker Ref. 8 * Newhouse N. W. Buerger
Maghemite Alameda County, California	Replaces titanium bearing magnetite to amount of 60–80%, 1–2% hematite present with oil immersion; residual magnetite is veined by numerous, minute veinlets of maghemite along octahedral planes. Very fine grained	Aggregate contains high ratio of Fe_2O_3 and 1.37% TiO_2. Microchemical tests show Ti in maghemite	Fine powder Bone brown	13″′ m	Greater than magnetite, less than hematite	White to gray blue. With oil immersion gray, like hematite	Isotropic. Some shows slight anisotropism	* Maghemite the chief constituent has cell edge a_0 8.32₆	Newhouse * N. W. Buerger
Maghemite, Windpass Mine, B. C.	Replaces non-titaniferous magnetite, as small veins to amount of 10–30%. Several per cent limonite present. Very fine grained	Aggregate contains high Fe_2O_3, the excess being about equivalent to the amount of maghemite observed in polished sections	Too fine intergrowth to obtain color of powder		Slightly greater than magnetite	White to blue gray	Masses too small to determine optical character	* Magnetite the chief constituent has cell edge a_0 8.36₉	Newhouse * N. W. Buerger

Posnjak,[9] also with the chemically analyzed maghemite from Bon Accord, Transvaal.[10]

For convenience of discussion some of the properties of these minerals from different places are given in tabular form.

X-RAY EXAMINATION.[11]

The minerals were ground to pass through a 200 mesh screen. A preliminary investigation was made using a Debeye powder x-ray camera. The results obtained with this method showed a real difference in the parameter values (a_0) of several of the samples. In order to obtain more accurate values than is possible with the Debeye method, the Phragmen high dispersion x-ray camera with CoK radiation was used.[12] The x-ray films thus obtained show differences in the lattice parameter values. The doublets were resolved in all but two of the films; in the case of these two films, however, good average values were used in calculating the parameters.

Microphotometer graphs of the film density were made in all cases. Values of a_0 were calculated from measurements made from these graphs.

	Cell Edge a_0	Notes
Magnetite		
Mineville, N. Y.	8.379	Nearly theoretically pure Fe_3O_4.
Magnetite (Titaniferous magnesioferrite)		
Magnet Cove, Ark.	8.371	Contains Al; Mg, Ti in solid solution.
Magnetite + small amount maghemite		
Windpass Mine, B. C.	8.368	The value given is that of magnetite, the maghemite being present in too small amount to give a pattern.
Magnetite + large amount maghemite		
Alameda Co., Calif.	8.328	Both magnetite and maghemite diffraction patterns were obtained. Only the latter cell edge given.
Maghemite		
Bon Accord, Transvaal	8.318	
Ferromagnetic		
Ferric oxide		Part of sample originally described by Sosman and Posnjak.
Shasta Co., Calif.	8.30	

[9] Mineral furnished through the kindness of the Geophysical Laboratory and E. Posnjak. See Ref. no. 2.

[10] Specimen kindly furnished by T. L. Walker, Royal Ontario Museum of Mineralogy.

[11] X-ray examination by N. W. Buerger.

[12] Westgren, Arne F.: X-ray determination of alloy equilibrium diagrams. Trans. Am. Inst. Min. Met. Eng., Inst. of Metals Div., pp. 14–17, 1931.

DISCUSSION.

Several lines of evidence suggest that maghemite varies in composition from $(FeTi)_2O_3$ to Fe_2O_3. Microchemical tests were made on small amounts of maghemite taken from polished sections of Bon Accord, and Alameda Co., Calif. Maghemite gave positive tests for titanium. Small lamellæ of ilmenite may have been included in the Bon Accord material. The evidence given by Walker also suggests its presence. The maghemite at Bon Accord replaces magnetite that without much doubt contained titanium in solid solution. This titanium would be expected to remain in the replacing mineral, or to form new separate compounds nearby. No compounds of that type were observed. The ilmenite lamellæ are of the type common to exsolution intergrowths of magnetite and ilmenite.

Although titanium in some amount is probably present in some of the occurrences, the maghemite from the Windpass Mine, B. C., can contain no more than a trace.

The microscopic estimate of the amount of maghemite present in the mixture of magnetite-maghemite from Alameda Co., Calif., was 60–80 per cent of the latter mineral. This agrees with the excess of Fe_2O_3 as determined by chemical analysis. A similar rough check was obtained on the material from the Windpass Mine, B. C.

It is obvious that there are some features held in common by the natural and artificial ferromagnetic ferric oxides and the maghemite from the several localities. It is equally obvious that certain differences also exist. All are ferromagnetic, but the artificial oxide differs from the others in magnetic characteristics.[13]

There is a color difference in polished section and considerable difference in hardness, and a marked difference in color of powder between the ferromagnetic ferric oxide from Iron Mountain, Calif., and maghemite from the several localities.

CONCLUSIONS ON MAGHEMITE.

Maghemite probably varies in composition from $(FeTi)_2O_3$ to Fe_2O_3. It is isometric with a crystal structure similar to mag-

[13] Sosman and Posnjak, pp. 335–337.

netite but with a smaller cell edge. The powder is dark brown (bone brown Ridgway), the polish hardness in section is above that of magnetite and below hematite. It is generally isotropic, and the color in polished section is white to gray blue, much like hematite. The x-ray work indicates that it is very fine grained. Fragments jump to a magnet in polished section.

HNO_3 neg., KCN neg., HCl neg., $FeCl_3$ neg., KOH neg., $HgCl_2$ neg. Zinc powder and HCl tarnishes maghemite, and develops structure. It may be formed by the replacement of titaniferous or nontitaniferous magnetite. It is found developed along fractures, grain boundaries, and along octahedral directions, in the magnetite, commonly in a very minute intimate network. Commonly a weathering product, it is doubtful if it is always so.

It is apparently not identical with the ferromagnetic ferric oxide from Iron Mountain, Shasta County, Calif.

SOME MAGNETIC PROPERTIES.

The magnetic work to be described was done by J. P. Glass in the Electrical Engineering Department, Massachusetts Institute of Technology, in 1933–34. Since that time improved methods and apparatus have been developed.[14] However, in view of the small amount of magnetic data that have been published on the powders of iron oxides of known identity, homogeneity, crystal or grain size, and chemical composition, it seems worth while to give the results obtained by Glass.[15]

Preparation of Iron Oxides for Tests.—Material was selected as free from visible impurities as possible. It was then crushed and screened so that it would all pass through a 100-mesh screen. Microscopic examination shows that the size of the crushed powder particle is below that of the average grain or crystal size of the original material (except the maghemite in the Windpass and Alameda Co. samples). This, of course, does not assure that the samples were all identical in gradation of size of particle.

[14] Dean, R. S., and others: U. S. Bur. Mines, Mineral Physics Studies, Rept. of Invest., 3268, 1935.

[15] (1) The magnetite from Sucasunny, N. J. Curve no. 2 in Figs. 2 and 3 was not adequately examined as to these features.

However, microscopic examination on glass slides and also in briquettes did not show any perceptible difference in proportion of very fine to coarser particles in the final samples (except for the maghemite). There also did not appear to be any difference in the proportion of different shapes of particle in the different samples. The powdered material was passed under an electromagnet of sufficient strength to pick up all the opaque mineral particles. The small amount of quartz, ferromagnesian silicates and feldspar remaining was discarded.

The magnetic examination and chemical analyses were made on these powdered samples, and microscopic examination was made of polished sections of the uncrushed minerals, and of briquettes containing the powdered minerals.

Magnetic Test Apparatus (*J. P. Glass*).—The material to be tested was placed in a brass cylinder about one half square centimeter in cross section area and 25 cm. long. This was placed in a heavy iron yoke to eliminate demagnetizing end effects and magnetized by a coil and storage batteries. In order to be sure that end effects could be safely neglected, tests were made with and without compensating end coils. The flux measurements were made by the ballistic galvanometer method, using a calibration coil of known dimensions for calibration. Proper compensation for flux through the exploring coil but not in the specimen was made in calculating the results. Thus the curves are true B–H curves for the mineral at the density of the packing used. The temperature of the specimen was controlled at $80 \pm 4°$ C., by the aid of a thermocouple, the magnetizing current being used for raising and natural cooling for lowering of the temperature. Since the accuracy of the work depended on the ammeters, the two used were selected from several after calibration with a potentiometer and standard resisters had shown them to be exceptionally accurate. These introduced no appreciable error in the results. About fifteen points were determined for each half loop of each of the hysteresis curves.

Magnetic Examination.—The features desired in the magnetic examination were that the results should be reproducible and that

the properties of one sample would be comparable with those of the others.

In preliminary tests it was found that results were reproduced when the same mineral density was maintained in the tubes. The convenient density of 3.25 gr./cm.^{3} was finally settled on as the standard (Fig. 1), it being the highest density to which all the specimens could be conveniently packed. Variations, which were seldom as much as 2 per cent., were caused by the difficulty of getting the mineral powders uniformly packed to identical density and possibly also to orientation of particles. Before packing in the test tubes the material was demagnetized by withdrawing the bottle of powdered mineral from a solenoid powerfully excited with alternating current.

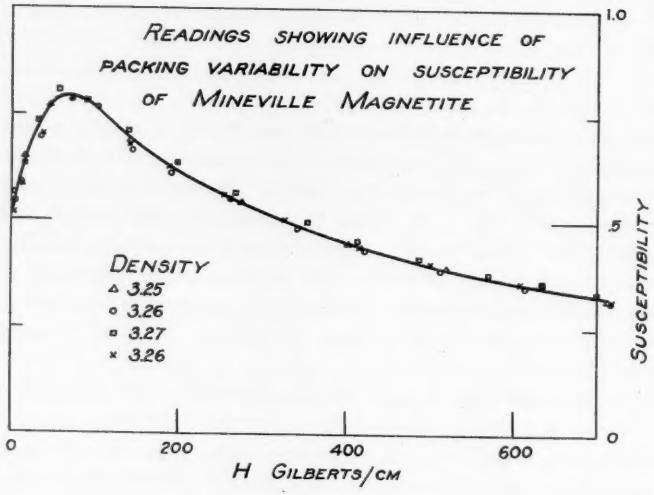
The material was then packed in the brass tubes by adding small amounts at a time with shaking or jarring until the tube was filled to the proper limit. Longitudinal shaking tended to produce laminations which caused a certain amount of difficulty. This lamination was greatly minimized by lateral jarring. After insertion of the sample in the apparatus, the material was again demagnetized by about 30 reversals of magnetizing current, the current being gradually decreased to zero. A number of trials were made to find out how many reversals were necessary to reach equilibrium at any point, and although no perceptible difference was obtained after the second reversal, as a precaution four reversals were always made before taking each reading.

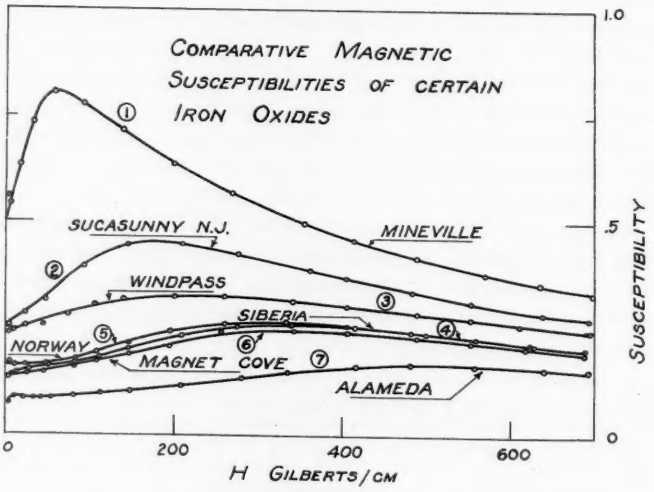
Discussion of Magnetic Data.—The data on susceptibility of Mineville magnetite are in good agreement with the results obtained by Slichter.[16] Loewinson-Lessing,[17] Koenigsberger[18] and others have shown that the thermal history of magnetite affects its magnetic properties.

[16] Slichter, L. B.: Certain aspects of magnetic surveying. Am. Inst. Min. Met. Eng., vol. on Geophysical Prospecting, p. 247, 1929.

[17] Loewinson-Lessing, F. von: Über die magnetische Verschiedenheit von Magnetitolithen Verschiedenen Ursprungs. Centralbl. f. Miner., Jer. A, pp. 369–377, 1932.

[18] Koenigsberger, J. G.: Die Abhängigkeit der natürlichen remanenten Magnetisierung bie Eruptivgesteinen von deren Alter und Zasammensetzung. Beiträg zur angewandten Geophysik, 5, 2, pp. 193–246, 1935.


READINGS SHOWING INFLUENCE OF
PACKING VARIABILITY ON SUSCEPTIBILITY
OF MINEVILLE MAGNETITE
DENSITY
△ 3.25
○ 3.26
□ 3.27
× 3.26
1.0
.5
0
SUSCEPTIBILITY
0
200
400
600
H GILBERTS/CM


COMPARATIVE MAGNETIC
SUSCEPTIBILITIES OF CERTAIN
IRON OXIDES
①
SUCASUNNY N.J.
MINEVILLE
②
WINDPASS
③
SIBERIA
④
⑤
NORWAY
⑥
MAGNET COVE
⑦
ALAMEDA
1.0
.5
0
SUSCEPTIBILITY
0
200
400
600
H GILBERTS/CM

FIGS. 1 and 2.

The thermal history (geologic) is not known for the material examined in the present study. Although of suggestive value only, it should be noticed that the magnetic properties of samples 4, 5 and 6 (titaniferous magnesioferrites) are very similar and show higher coercive force and remanence than Mineville magnetite. These each contain considerable amounts of Ti, Mg and Al. The aggregates of magnetite and maghemite (curves 3 and 7) have higher remanence and coercive force than Mineville magnetite (ordinary magnetite almost ideal Fe_3O_4). The x-ray work has emphasized strongly the very finely divided nature or fine grain of the maghemite investigated in the present study. Thus, oxidation has produced a large interface. Recent work by Dean, Gottschalk, and Davis[19] indicates that coercive force increases with interface, i.e., with decrease in grain size.

Although the influence of other possible factors can not be denied, this new evidence suggests that under certain conditions of oxidation, magnetite is oxidized partly to maghemite, with the formation of a large interface and consequent high coercive force. This would seem to be the origin of one of the materials from which "lodestone" may be formed.

Since maghemite has also been found distributed through lavas where it replaces magnetite,[20] it should be of interest to the geophysicist dealing with ferromagnetism in the earth's crust.

SUMMARY AND CONCLUSIONS

A mineral with the properties and occurrence of maghemite has been found replacing magnetite from a number of localities. This mineral replaces titaniferous magnetite as well as nontitaniferous magnetite and the evidence suggests that its composition varies from $(FeTi)_2O_3$ to Fe_2O_3. The maghemite from the

[19] Dean, R. S., and others: *Op cit.* Davis, C. W.: Geological significance of magnetic properties of minerals. ECON. GEOL., vol. 30, pp. 656–661 (1935).

[20] Nieland, H.: Beitrag zur kentnis der Deckenbasalt von Westgronland. Chemie der Erde, vol. 6, p. 596, 1931. Odman, O. H.: Mineragraphic study on the opaque minerals in the lavas from Mt. Elgon, British E. Africa. Geol. Foern. Stockholm, Forhand, pp. 296–298, 1932. Newhouse, W. H.: Opaque oxides and sulphides present in common igneous rocks. Geol. Soc. Am. Bull., vol. 47, p. 11, 1936.

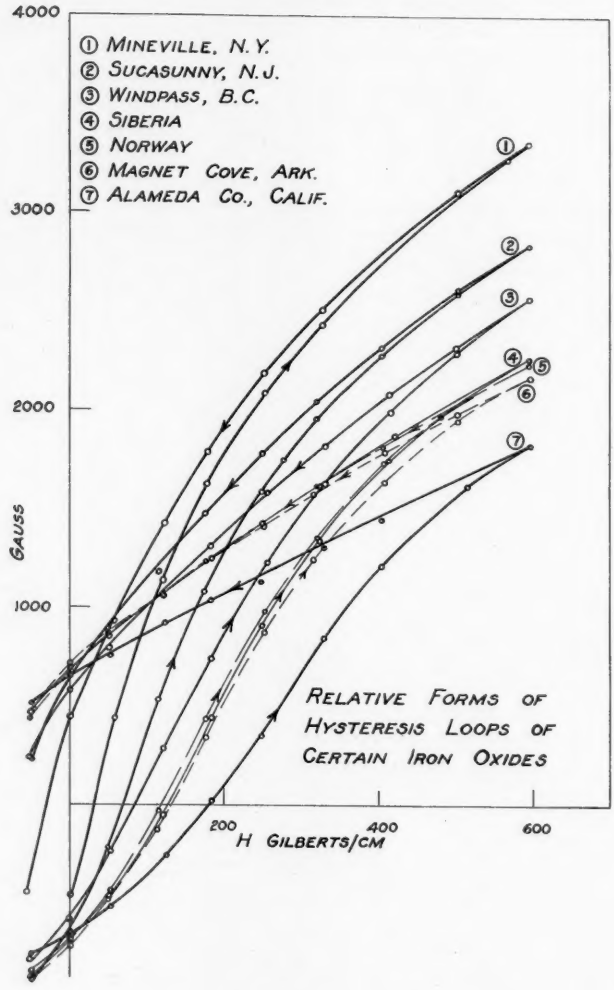

4000
3000
2000
1000
GAUSS
① MINEVILLE, N.Y.
② SUCASUNNY, N.J.
③ WINDPASS, B.C.
④ SIBERIA
⑤ NORWAY
⑥ MAGNET COVE, ARK.
⑦ ALAMEDA CO., CALIF.
RELATIVE FORMS OF HYSTERESIS LOOPS OF CERTAIN IRON OXIDES
200
400
600
H GILBERTS/CM

FIG. 3.

three occurrences examined was all very fine grained as was shown by x-ray diffraction pattern lines. It may commonly be a weathering product but its occurrence widely in one type of lava suggests that it may also be formed by certain hydrothermal, or late magmatic processes. It is not identical with the ferromagnetic ferric oxide from Iron Mountain, Shasta County, Calif., which was first described by Sosman and Posjnak, but in some respects corresponds to that mineral.

The magnetic work of one of the authors (Glass) indicates a high coercive force for ("lodestone"), maghemite-magnetite, from the Windpass Mine, B. C., and from Alameda Co., Calif. A high coercive force has also been found by Davis [21] on an "oxidized type" of lodestone from Alameda County that contained 90.47 per cent. Fe_2O_3. It is suggested that the explanation of the high coercive force lies in the fine-grained structure. This fine-grained structure was produced in the present material by oxidation of a special type.

ACKNOWLEDGMENTS

Thanks are due to Professor C. E. Lansil of the Electrical Engineering Department who supervised the work on magnetism, and to Professor M. J. Buerger and N. W. Buerger for the x-ray work.

MASSACHUSETTS INTITUTE OF TECHNOLOGY,
CAMBRIDGE, MASSACHUSETTS,
August 2, 1936.

[21] *Op. cit.*, p. 95.

ORIGIN OF THE SOUTHEASTERN MISSOURI LEAD DEPOSITS. PART I.

W. A. TARR.

THE origin of the lead deposits of southeastern Missouri has long been, and still is, one of the difficult problems in ore deposition. Simple in mineralogy and mode of occurrence and lacking in evident association with igneous rocks that might have played a part in their origin, these deposits furnish little evidence that supports, strongly, any one of the common interpretations of the origin of such mineral deposits. This very simplicity, however, because it fits so readily into the general features (*not* the details) of more than one possible mode of origin, has allowed two widely divergent views to become adopted as probable explanations. What—according to one group of students—could be a more simple and accurate explanation than that meteoric waters in passing through the rocks (adjacent to the present deposits) should have acquired the lead, iron, sulphur, and associated metals, and then later redeposited them in the dolomite (in which the lead ores occur). There are no closely (or even remotely, according to some writers) associated igneous rocks; no silver occurs in the ores; numerous other metallic elements often found with lead associated with igneous rocks are consistently absent; and the country rock, dolomite, is readily replaceable. All these are points that work nicely into the concept of deposition by meteoric waters. The other group of thinkers, however, recognize the chemical limitations of cold meteoric waters to transport the normally very insoluble lead salts and doubt the adequacy of the assigned source of the lead and sulphur. They think, therefore, that the deposits are due to magmatic waters with their greater chemical ability to transport and deposit lead salts, as well as to accomplish replacement. Making use of the evidence (which is steadily accumulating) that magmatic waters penetrate thousands

of feet from the parent rock, these men find the mineralogy and mode of occurrence of the Missouri deposits more in accord with an origin due to magmatic waters.

The evidence of the minerals, alone, has hitherto been singularly lacking in diagnostic value. The replacement of a dolomite does not impose insuperable difficulties upon even a cold weak solvent such as most meteoric waters are. The occurrence of disseminated replacement and vein deposits is a common feature wherever waters permeate rocks and deposit minerals. A review of the existing literature reveals a modicum of evidence presented for either interpretation.

Faced with this simplicity in the elemental factors so commonly used in support of a particular theory and the further ease of their utilization in support of either of the prevalent views of origin, how must the student proceed in an attempt at the solution of the problem? The most satisfactory method, as the writer sees it, is a careful analysis of every step involved in the origin. The literature reveals the fact that some points have been analyzed with much care while just as vitally related points were ignored. One author has devoted much space to the source of the lead but has handled its transportation and deposition inadequately (the treatment of these two last factors is a common weakness in most statements of the origin). Another has emphasized the means of entrance of the mineralizing solutions, and another the mode of occurrence. No one doubts that all the steps in the sequence are related; yet, with the limitations placed upon us by our lack of knowledge of the details of the processes going on in the rocks (much of our knowledge results only from the assumption that principles determined in the laboratory do apply to earth processes), following a sequence in detail may soon become a record of the investigator's beliefs rather than a purely scientific account. A sequence, however, the details of which are related, based upon laboratory work, and applied within the range of limitations determined in the laboratory, has great value and may be kept relatively free from mere belief. Then, it is permissible that the

investigator pass into the realm of interpretation, as others may do also from a perusal of the evidence he has presented.

For more than 20 years, the writer in his study of the lead ores of Missouri has been collecting data in the field, laboratory, and literature, and in this paper presents the results of his study. As the study progressed and its phases were isolated and examined, it became increasingly evident that the simplicity, noted above, demanded extremely careful detailed study for each phase if the most probable interpretation was to be made. The writer will present an analysis of the origin of the lead deposits, along with certain new factors his work has revealed that appear to be significant in explaining that origin.

His thanks are extended to the committees on "Ore Deposition" and "Grants" of the National Research Council for financial aid in pursuing the work. He also wishes to thank Messrs. P. A. Haines, R. E. Wagner, L. P. Pressler, and other members of the staff of the St. Joseph Lead Company for their unstinted aid throughout the progress of the work. Mr. Wagner's aid underground and in studies of the diamond-drill cores, as well as his criticisms during numerous discussions of the problem, has greatly facilitated the study. Thanks are also due to Professor W. A. Albrecht of the soils department of the University of Missouri for a bacteriological test of the ores.

LOCATION OF THE DEPOSITS.

The lead deposits of southeastern Missouri occur in St. Francois, Madison, Iron, and Washington counties. The term "lead belt" is commonly applied to the St. Francois County deposits, which are the largest and most important, but important mines occur also near old Mine La Motte (where lead was discovered in 1720) and Fredericktown in Madison County, and near Annapolis in southern Iron County (Fig. 1). Barite is the chief mineral mined in Washington County, at present, but this area was the leading producer of lead in the region 125 years ago. Schoolcraft[1] gave an excellent account of these mines in 1819.

[1] Schoolcraft, H. R.: The Lead Mines of Missouri. Charles Wiley and Co., 1819.

Today, any galena found with the barite is saved and sold. At present only the mines at Flat River, Leadwood, and Bonne Terre in the "lead belt" are being operated.

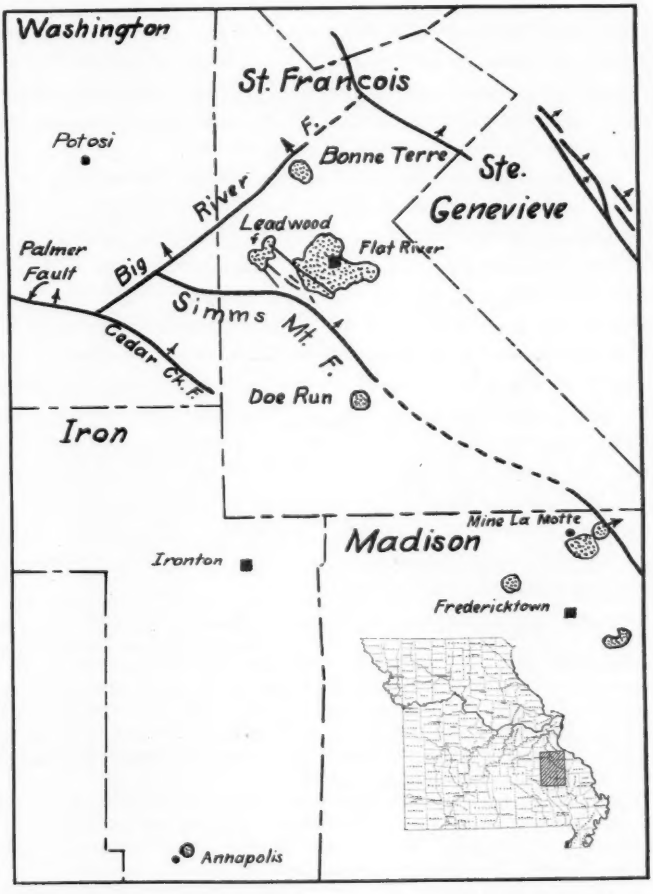


FIG. 1. Map showing location of lead deposits (stippled areas) and major faults of area. Insert shows location of lead district in Missouri.

GENERAL GEOLOGY.

Because the geology of the area is comparatively simple and good descriptions of the formations are available,[2] only the new details brought to light during this study will be emphasized. The lower Paleozoic sediments (in which the lead ores occur) rest upon pre-Cambrian igneous rocks. The latter are exposed in the central part of what was originally a low dome (later modified by faulting and gentle warping). The important lead deposits occur entirely in the Cambrian formations.

Igneous Rocks.—The pre-Cambrian basement consists of a series of rhyolitic (and andesitic) porphyries into which several granites have been intruded.[3] Both porphyry and granite have, in turn, been cut by diabase dikes. The latest igneous rocks are peridotite necks, which are Paleozoic or later in age. The porphyries and granites are exposed to the south and southwest of the lead deposits and to the northeast in Ste. Genevieve County. The former is the largest area of exposed igneous rocks in Missouri. Porphyry, evidently in the form of buried hills, has been encountered in the mines. The peridotite dikes (which cut the Cambrian, and one of which, at any rate, has been shown to be at least post-middle Devonian in age) [4] occur in a group within a few miles of each other, about 12 to 15 miles southeast of Flat River. With one of these necks (an alnoite, near Avon, Missouri), a small deposit of sulphides is associated.[5]

[2] Winslow, Arthur: Lead and Zinc Deposits of Missouri. Mo. Geol. Surv., vol. 7, pt. 2, 1894. Buckley, E. R.: Geology of the Disseminated Lead Deposits of St. Francois and Washington Counties, Mo. Mo. Bur. Geol. and Mines, vol. 9, pts. 1 and 2, 1909. Haworth, E.: The Crystalline Rocks of Missouri. Mo. Geol. Surv., vol. 8, 1894. Spurr, J. E.: The Southeast Missouri Ore-Magmatic District. Eng. and Min. Jour., vol. 122, pp. 968–975, 1926. Lindgren, W.: Mineral Deposits, pp. 438–441, 1933. Dake, C. L.: The Geology of the Potosi and Edgehill Quadrangles, Mo. Mo. Bur. Geol. and Mines, vol. 23, 1930.

[3] Tarr, W. A.: Intrusive Relationship of the Granite to the Rhyolite (Porphyry) of Southeastern Missouri. Geol. Soc. Am. Bull., vol. 43, pp. 965–992, 1932.

[4] Tarr, W. A., and Keller, W. D.: A Post-Devonian Igneous Intrusion in Southeastern Missouri. Jour. Geol., vol. 41, pp. 815–823, 1933.

[5] Ball, S. H., and Singewald, J. T., Jr.: An Alnoite Pipe, its Contact Phenomena and Ore Deposition near Avon, Mo. Jour. Geol., vol. 38, pp. 456–459, 1930. Singewald, J. T., Jr., and Milton, Chas.: An Alnoite Pipe, its Contact Phenomena and Ore Deposition near Avon, Mo. Jour. Geol., vol. 38, pp. 54–66, 1930. Spurr,

Sedimentary Rocks.—The sedimentary rocks in which the lead ores occur are all Cambrian in age, although in central and southwestern Missouri lead and zinc occur in later Paleozoic formations. The following formations are recognized in the region as members of the Cambrian and Ordovician:

		Maximum Thickness in Region.
	Roubidoux sandstone and dolomite	100 feet
Ordovician	Gasconade dolomite	140 "
	Van Buren dolomite and sandstone	80 "
	Eminence dolomite and chert	200 "
	Potosi dolomite	400 "
	Derby-Doerun formation	120 "
Cambrian	Davis shales	180 "
	Bonneterre dolomite (ore horizon)	450 "
	La Motte sandstone	240 "
	Unconformity at top of pre-Cambrian igneous rocks.	

Cambrian Formations.

La Motte Sandstone.—The La Motte is a medium- to fine-grained white sandstone, normally very pure and with well rounded quartz grains. Local phases contain shale and are red and green. In some localities, a conglomerate composed of porphyry pebbles, some of which are six inches in diameter, occurs. The beds of the sandstone range from one-quarter of an inch to several feet in thickness. Cross-bedding is common.

Bonneterre Dolomite.—As the Bonneterre dolomite is the chief ore horizon of the district, its petrographic details are of especial significance. The formation is normally a very pure dolomite as the following analysis shows:

ANALYSIS (PARTIAL) OF BONNETERRE DOLOMITE.[6]

$MgCO_3$	39.54 per cent.
$CaCO_3$	55.41 " "
Al_2O_3, Fe_2O_3	1.76 " "
SiO_2	3.26 " "
	99.87 per cent.

J. E.: The Southeast Missouri Ore-Magmatic Region. Eng. Min. Jour., vol. 122, pp. 968–975, 1926.

[6] Buckley, E. R.: *Op. cit.*, p. 43.

Certain beds, however, contain glauconite, sand, or shale. The glauconite (erroneously called "chlorite" in Winslow's and Buckley's report) is confined largely to the lower 50 feet of the formation, though it may occur higher up. Some beds are 90 per cent. glauconite, and many contain 30 to 40 per cent. It occurs as well rounded grains as large as ⅛ inch in diameter, and as small grains and powder. The lower part of the dolomite is commonly distinctly sandy and may even contain thin sandstone layers. A conglomerate bed (maximum thickness 12 inches) with rhyolite-porphyry and granite-porphyry pebbles and cobbles (attaining 5 inches in diameter) occurs in the Rivermines area just south of Flat River. This bed is 50 feet or more above the base of the Bonneterre and about two miles from the porphyries to the south (although the pebbles may have been derived from a nearby, though buried, porphyry hill). Higher up in the formation occur isolated small pebbles which, as they are well rounded, evidently represent ice rafting off shore. The cores from diamond drills have revealed the presence of such a zone about 235 feet above the base of the Bonneterre. This zone is about 30 feet thick and contains pebbles of porphyry reaching two inches in diameter. Small angular porphyry and quartz gravels (less than ⅜ inch in diameter) occur also along certain horizons near the base of the formation. These undoubtedly also originated through ice rafting.

The sand grains in the dolomite are nearly always perfectly rounded, have a mat surface, and are from .01 to .05 inch in diameter. If small in amount, they are scattered through the dolomite. Thin (up to .75 inch) lenticular siltstone layers (see Fig. 8) occur near the base of the Bonneterre. Oölites are found throughout the dolomite, but are abundant only in the lower part of the 130-foot zone, described below.

It is especially important to note that the Bonneterre dolomite is singularly free from shale layers, as their presence is significant according to earlier views of the origin of the lead deposits. Much, if not most, of this supposed shale is the insoluble residue of the dolomite that has accumulated along solution planes. The

thickest shale layer seen by the writer was about two inches, but Mr. Wagner has observed layers that are somewhat thicker. There are more shaly-dolomite layers than shale layers, but the former, also, are thin. Although called "shale" these layers consist mostly of a mixture of silt and clay, with the silt size more abundant. All these shaly phases are dark gray to nearly black in color. There are many thin (⅜ inch or less) dark shaly layers (Figs. 4, 9, and 11) throughout the formation, and especially in the lower 100 feet, but (as will be shown below) they consist of residual materials along planes where solutions have removed the dolomite.

The Bonneterre is generally some shade of gray, ranging from nearly white to almost black. The dark colors are due chiefly to carbonaceous material, though in some phases the coloring material is a finely divided black sulphide. An irregular distribution of the coloring material gives a mottled appearance to some parts of the formation. Pink and buff layers are not uncommon, and the layers containing glauconite range from a light to a dark green, depending upon the quantity of glauconite present. Oxidation along water channels and along certain beds has given them a yellow color.

The Bonneterre generally contains a gray sand at its base. A glauconitic (also sandy) zone, from almost 0 to 50 feet thick, is generally found in the lower part of the formation. An 80-foot zone (an important ore horizon) above the glauconite beds commonly shows numerous stylolitic seams and solution planes. Near the base of this zone there is a brown, spotted phase. In some drill cores, this 80 feet of material is a tan, granular dolomite with a much smaller number of stylolites or solution planes.

Another well marked zone (125–135 feet thick) immediately above the 80-foot zone is characterized by numerous color variations (dominantly a gray-spotting) and the presence of slender finger-like columns (Fig. 2). This remarkable structure is best described by Mr. Wagner's name, "fingered rock." The "fingers" are some shade of gray, pink, or red, and normally are ¾ to 1½ inches (2 to 4 cm.) in diameter and from 3 to 12 inches

(8 to 20 cm.) in length; rarely, they are several inches in diameter and may taper upwards or downwards. They suggest long slender stylolitic columns, but although they are nearly uniform in diameter their sides have numerous reëntrants which never appear on the sides of stylolites. The sides of the fingers are

FIG. 2. The fingered rock. "Fingers" at right (lighter-colored, elongated areas with irregular boundaries) and at left center. 2/3 natural size.

apt to be wavy; in fact, they bear some resemblance to stylolitic seams in a vertical position. The fingers occur in a gray dolomite and possess the same textural features as the surrounding rock. The dolomite between the fingers may be the same width as the fingers, or it may be wider. The contact between the fingers and adjacent dolomite is marked by a very thin band of marcasite. The gray dolomite contains much scattered marcasite in patches of variable shape. The reddish or pink fingers may contain some patches and a few scattered grains of marcasite, but normally they are essentially free from it. The reddish color is

due to the presence of ferric oxide. These facts suggest that the fingers represent changes produced in the original dolomite by the ore solutions that changed the sulphide, and oxidized parts of the iron to ferric oxide. The fingered beds are mostly from a foot to several feet in thickness and are scattered throughout the 130 feet of beds in which some ore occurs. Well developed oölitic beds occur in the lower part of this zone.

The Bonneterre formation is well bedded, and the present beds range in thickness from 4 to 5 feet down to an inch, or even less where many stylolitic seams are present. Their original thickness was probably greater. The present evidence of bedding is indicated chiefly by stylolitic seams and solution planes; it is doubtful whether an original, unmodified bedding-plane could be distinguished in the entire formation. Other evidences of bedding are shown by the glauconitic, sandy, shaly, and siltstone layers, although stylolites are commonly developed, also, at their contact with adjacent beds. Textural differences, likewise, indicate different beds.

The texture of the formation ranges from coarse (using the size scale for clastic particles, *i.e.*, ⅛ inch or 2 to 3 mm.), through medium grained, to fine grained (.04 inch) and very dense. The rock is always crystalline, and the grains are mostly anhedral and range from equigranular to inequigranular. Normally, all constituents are fresh, although some of the phenocrysts in the porphyry pebbles are evidently altered to kaolinite, and certain beds of dolomite have apparently been bleached and possibly recrystallized by the ore solutions. The included glauconite, sand grains, and small pebbles are surrounded by the dolomite grains.

The Bonneterre dolomite has a wide variation in porosity (Fig. 3), and this porosity is a factor in the distribution of the ores. The dense layers show a little evidence of porosity in the form of rare minute cavities and still rarer replacement by sulphides. The apparent porosity determined for such a rock showed only .78 per cent. The fine- and medium-grained rocks all show intergranular pore space amounting to two or three per cent. The coarse-grained (and occasionally the medium-grained)

rocks show a remarkable number of cavities and intergranular openings. Water passes through these rocks readily, although many of the cavities are not connected with other openings. These rocks have an apparent porosity of 3 to 10 per cent. The distribution of the sulphides (especially galena, but also the marcasite) shows that any phase, from fine to coarse grained, was permeable by the ore-bearing solutions. The numerous cavities

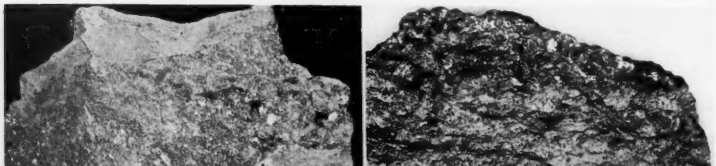


FIG. 3 (Left). Bonneterre dolomite showing variations in porosity. Galena (white spots) is in coarser phases. 2/3 natural size.

FIG. 4 (Right). Bonneterre dolomite with numerous stylolitic seams and other solution planes. Note irregular patches of dolomite separated by stylolitic seams in lighter-gray portion, and numerous solution planes in dark portion which consists largely of residual clay. White spots are galena. 2/3 natural size.

of the Bonneterre are from .004 inch to 2 inches in diameter. They are lined with small dolomite crystals and are, therefore, called "druses." Their shape is mostly irregular, but tubular forms are surprisingly common. These tubes range from .002 inch to .125 inch in diameter and may be an inch in length. They are dominantly vertical though they may lie in any position. These drusy cavities are not connected with each other, as a rule; hence are not passages for solutions. They are most abundant

in the more porous layers, but occur in any type of dolomite. There are larger openings (some several inches across) that are evidently due to solution. These openings generally show a drusy lining of dolomite crystals, and although similar to the vugs in veins are really druses.

The Bonneterre contains only a very few fragmentary fossils, chiefly of linguloid forms. They occur mainly in the lower part of the formation. A number of beds show circular (often dark) and elliptical areas strongly suggestive of some organic form.

The most striking feature of the Bonneterre dolomite is the great number of stylolites, stylolitic seams (*i.e.*, columns not clearly defined and sometimes called "suture joints"), and residual clay partings (Fig. 4). As mentioned above, it is the presence of these features that emphasizes the bedded character of the rock. As all these features normally develop along (or parallel to) bedding planes, their present position is presumably indicative of the original bedding. The stylolites rarely exceed an inch in length, which represents the amount of differential solution. The stylolitic seams do not exceed ½ inch in length, and range down to seams so minute that 100 are included in the space of one inch. Twenty or 30 seams to the inch are not uncommon. The residual clay partings may be nearly one-half inch thick. Determinations of the insoluble residues of the dolomite showed that the amount varied widely, just as would be expected; the percentages ranged from 1.7 to 10.4. This insoluble residue was concentrated along the stylolitic seams, showing that much dolomite had been removed in solution. Stockdale's[7] estimate of 30 or 40 per cent. of the rock removed would probably be too low for some parts of the Bonneterre dolomite. Even the surfaces of the stylolitic seams may show the slickensided and striated character of the stylolite columns.

Though normally parallel to the original bedding, the stylolites and stylolitic seams may cross the beds at all angles, nearly to 90°. Their criss-crossing has woven an extremely complex pattern in

[7] Stockdale, P. B.: Stratigraphic Significance of Solution. Jour. Geol., vol. 34, p. 407, 1926.

many parts of the formation, producing in some beds a distinctly brecciated appearance. Most stylolites and seams have an undulating character which adds to the complexity of the pattern.

Some structures, well shown in the Bonneterre, suggest gigantic stylolites. As seen in the mine, they are undulating seams consisting of residual clay, commonly 1 inch thick, with a maximum vertical range of 30 inches. The rock below the seam has a ridge-like appearance. The rock above usually curves over these ridges, as is shown by the stylolites and stylolitic seams it contains, but the rock below shows horizontal stylolites crossing the

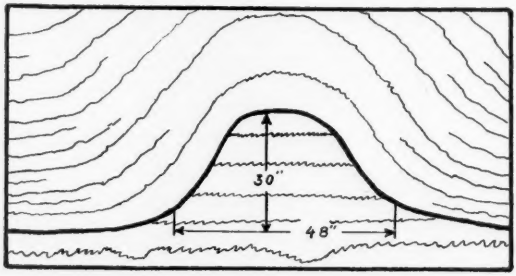


FIG. 5. Sketch of a ridge (seen in mine) with horizontal stylolitic seams and other beds (also with stylolitic seams) arched over it. Due to removal of dolomite on each side by development of stylolites.

ridge (Fig. 5). The sides of the ridges and inclined portions of the seams show the usual stylolitic striations. Some of the smaller of these ridges (3 to 6 inches high) have a rude symmetrical arrangement which strongly resembles that of ripple marks. These gigantic stylolites (?) originated in the same manner as the smaller stylolites.

Another remarkable structure, also related to solution work, consists of columns, as large as 6 feet across, that are separated by nearly vertical joints toward which the beds in the columns dip. The downward flexure of the beds at the joints may be from 12 to 15 inches, which gives the columns the appearance of nested saucers upside down. All these stylolitic features and other evidences of solution work will be discussed later under "origin."

Larger structural features, such as cross-bedding and ripple marks, are consistently absent in the formation, although, as stated above, certain parallel ridges resemble ripple marks.

Davis Shale.—Although commonly called a "shale," the Davis formation contains also many beds of dolomite and limestone (two are oölitic), some conglomeratic limestones and dolomites, no less than eight edgewise conglomerates, and a bed of large (several feet across) limestone boulders about 60 feet from the top. Moreover, parts of the formation contain lenses and layers of sandstone and some of the shale and dolomite shows disseminated sand grains. The Davis is quite distinctly calcareous, and glauconite is common in all parts. Ripple marks and mud cracks are common, and fossils are abundant in certain layers. There are no ores in the formation.

Derby-Doerun Formation.—The Derby-Doerun formation consists primarily of dolomite, but the lower 40 feet (Derby) is calcareous, and the upper 50–60 feet is argillaceous, especially so in the lower two-thirds of this part. The upper part shows cross-bedding and numerous quartz-lined druses.

Potosi Dolomite.—The Potosi dolomite consists of massive beds (maximum thickness, 4–5 feet) of dolomite with abundant quartz (and chalcedony) lining druses and geodes. Present also are layers (2–3 feet thick) of tubular quartz druses and geodes, the tubes being an inch or more in diameter with the crystals on the outside and the dolomite inside. There is also much chert in the formation. The Potosi has a fine- to medium-grained texture, is some shade of gray or brown in color, and weathers to a deep red soil. Its outcrops lie to the south, west, and northwest of the lead belt proper. Most of the production of barite (along with some galena) in Washington County comes from the Potosi formation. These important barite deposits lie about 10 miles to the northwest of the lead belt.

Eminence Dolomite.—The Eminence dolomite is not found in the lead belt but is widespread to the west and southwest of the area. It is a very cherty, light gray, crystalline, massive (below) to thin-bedded (above) dolomite. It attains thicknesses of 200

feet. The chert it contains occurs as nodules, lenses, and beds (some of which are several feet thick). The Eminence comprises the top of the Cambrian.

Ordovician Formations.

An unconformity separates the Ordovician from the Cambrian. The Van Buren, Gasconade, and Roubidoux formations are found in the area to the west of the lead belt but no important deposits of either lead or barite are associated with any of them. Their total thickness is about 320 feet. They consist of dolomite, chert, and sandstone, with practically no shale. The amount of chert (in beds, maximum thickness 3–4 feet) is enormous. Only in the Roubidoux does sandstone become abundant. Ripples and mud cracks are common in all the formations.

STRUCTURAL GEOLOGY.

The major structural element of the region of the Missouri lead deposits is the gently sloping dome formed by the Paleozoic sediments surrounding the pre-Cambrian igneous rocks of the St. Francois Mountains. These sediments lie among pre-Cambrian hills, and at a distance from the igneous center completely bury them. The sediments dip away from the igneous rocks into the valleys between the hills, and thus have a synclinal structure. The dip of the beds ranges from a very slight one to 20°; that around a porphyry hill in the Bonne Terre mines is 400 feet in a mile. Where the pre-Cambrian hills were some distance apart, these initial dips soon flatten out and the sediments become essentially horizontal. Where the sediments have buried a hill, a dome results, and the structure may continue into the overlying Davis formation about 350–450 feet above. The contact of the La Motte sandstone with the Bonneterre dolomite is undulating, which produces differences in elevation of the La Motte surface amounting to 30 or 40 feet. These rolls of the surface are minor structural features, but were probably important in the deposition of the ores.

The original position of these Paleozoic sediments has been disturbed by subsequent movements, primarily, faulting but also gentle folding and uplift. The major faults are northwest, north, northeast, and east of the igneous rocks (Fig. 1), although faulting in some degree doubtless occurs entirely around (and within) the pre-Cambrian area.

Faulting.—The Simms Mountain ("Irondale" of Buckley) fault strikes N. 65° W. across the area and about 4 or 5 miles to the southwest of Flat River. Its maximum displacement is about 600 feet, with the downthrow side on the northeast. It is nearly vertical. A reconnaisance survey indicates that the Simms Mountain fault extends to the southeast and becomes a part of the Mine La Motte fault system in Madison County (a view also concurred in by Dake [8]). The Mine La Motte fault has a displacement of at least 300 feet with the downthrow side to the northeast, and has a course that is in alignment with the Simms Mountain fault. In Washington County about five miles southwest of the Simms Mountain fault is Cedar Creek fault, paralleling the former and like it having the downthrow side on the northeast. Its displacement is about 400 feet. This fault, as the "Palmer fault zone," is continuous to the northwest across Washington County where it has a maximum displacement of 800 feet.[9]

Big River fault (named from the river to the west of which it lies) strikes N. 40° E. with the downthrow to the northwest. It begins at Cedar Creek fault, cuts the end of the Simms Mountain fault, and doubtless ends at the great fault zone in Ste. Genevieve County to the northeast. Big River fault has a maximum displacement of about 120 feet.

Originally, the block lying between the Simms Mountain and Big River faults dipped gently northeast, but the Simms Mountain fault carried the southwest end of it down until the present dip is gently in that direction. A broad low anticline to the east of Flat River and Farmington aids in accentuating this southwest

[8] Dake, C. L.: *Op. cit.*, p. 182.

[9] Dake, C. L.: (*Op. cit.*, p. 183) describes a cross fault in this zone of probably 1,200 feet.

dip. It will be noted that the mining districts (Fig. 1) are not far removed from the large faults which limit this fault block.

There are many small faults that cut the ore bodies throughout the mines. Most of them have a displacement of a few inches to a few feet, but some show a movement of 20 to 40 feet, and in the Flat River district, one, the Shultz, with a northwest strike, has a displacement of 100 $\pm$ feet. This and several other important faults roughly parallel the Simms Mountain fault. There is a northeast-southwest fault zone (with from 80- to nearly 100-feet displacement) in the southeastern part of the Flat River area. Smaller faults may parallel the major faults or lie at various angles.

There is an important point in connection with the faulting of the region that should be considered. The Paleozoic sediments rest upon the pre-Cambrian basement of igneous rocks and are relatively thin, probably 500 to 600 feet in the mining districts and slightly less than 1,000 feet in most of the area, hence any fault with a displacement of 100 feet (or even less) would undoubtedly also *cut* the pre-Cambrian. Evidence of faulting is abundant throughout the pre-Cambrian igneous area, but little is known as to the amount. The question is whether the post-Cambrian faults are continuous with pre-Cambrian faults. Undoubtedly, for the most part they are, so any marked displacement of the Cambrian (or other) beds involves the igneous basement below. There are also undoubtedly many faults in the pre-Cambrian formations that have no counterpart in the overlying sediments, as pre-Cambrian rocks elsewhere show faults that strike and dip in all directions.

Joints.—The sedimentary rocks contain many joints, some of which are sufficiently persistent to cross the entire thickness (about 450 feet) of the Bonneterre dolomite. From these prominent joints, they range in size downward until they fade out. The persistent joints are commonly sufficiently open (probably due, in large part, to solution work) to form water channels, from which variable quantities of water flow into the mines. The surface connection of many of these water channels is shown

by the fact that their water flow fluctuates with the rainfall. Also, the walls of the channels show that the solutions are oxidizing solutions and hence probably of surface origin. It is not uncommon to find equally persistent joints parallel to and near the water channels but so tight that they are dry or show only water seeps. Smaller joints may also act as water courses, but this is not common.

The igneous rocks are much jointed, especially the porphyries, which are intensely shattered in places. The granites (which are younger than the porphyries) are much freer from joints. That similar joints are present in the pre-Cambrian igneous rocks under the sediments can scarcely be doubted.

The majority of the joints in the district (as determined by Buckley who devoted much time to their study) strike from nearly east-west to N. 50° W. A less prominent group strikes N. E. and S. W., largely between N. 30° to N. 80° E. There are also joints in other positions, but the above include the most important. The major joints are nearly vertical and most of the others approximate that position, but there are also many small diagonal joints that dip 50 to 90°. The presence of these various joints is readily determined by their mineral content. In local areas, the shattering has been so intense that the dolomite appears to be brecciated.

Stylolites and Bedding Planes.—Ranking with the faults and joints of the area as important structural elements that have played a part in the mineralization are the stylolites and bedding planes. These features have already been described under the discussion of the Bonneterre dolomite, but they must be mentioned here also. It is doubtful (as stated above) whether an original unaltered bedding plane occurs in the Bonneterre, since the bedding planes are now represented by the stylolites and other solution features. The bedding planes, originally present, were the means of entrance for the ground water, which they guided laterally into the dolomite. Solution work followed and the stylolitic and other solution planes developed. As bedded and disseminated ores predominate in the mines, the significance of

this ingress of solutions is evident. Bedding planes are well developed in the underlying La Motte sandstone, but they are not, nevertheless, important as channels for the movement of water since the sandstone is very porous and readily permeable to solutions in any direction.

The development of the stylolites and solution planes began as soon as the Bonneterre was a firm rock (stylolitic seams are common in chalk), and has undoubtedly continued down to the present. In other words, they are both pre- and post-mineralization, unless the mineralization occurred immediately after the deposition of the dolomite, which is doubtful. Wherever differential pressure existed along a bedding plane, stylolites or stylolitic seams might develop. If the pressure was uniform, solution would be uniform on one or both sides of the bedding plane and a solution plane would result. All these solution features show a residual deposit of a dark clay-like material. It is probable that horizontal clay partings have been interpreted as bedding planes by past observers. The solution features were developed also within the beds, and even followed diagonal courses. Although they developed, for the most part, below ground-water level, there were undoubtedly periods of active growth during the Paleozoic, Mesozoic, and Cenozoic eras when the physiographic conditions of the region were such as to cause a more rapid circulation of the water. As is true of the stylolitic features of other carbonate rocks, the solutions developing the stylolites were not oxidizing solutions, as neither the residual material nor the rock containing the stylolites shows evidences of oxidation. The number and size of these solution features suggest the removal of much material, as will be shown later.

THE LEAD DEPOSITS.

The southeastern Missouri region has been one of the world's leading lead producers for half a century and at the apex of its production it led the world. The area still has enormous reserves of workable ore. The ore mineral is galena, accompanied by marcasite and minor amounts of other sulphides. The Missouri

Cobalt Mine at Fredericktown has a different mineralogy from that of the other mines, as will be noted later.

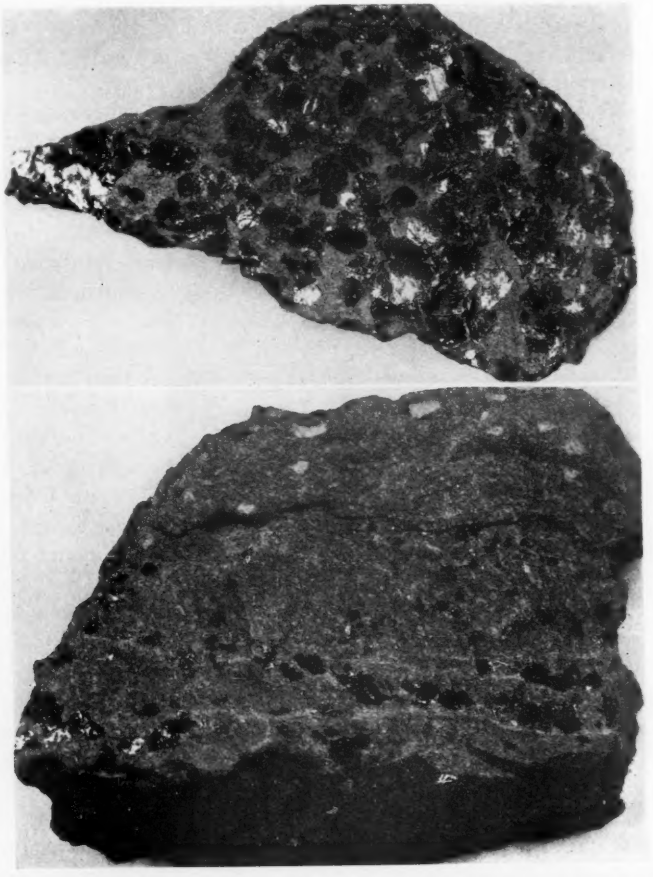


FIG. 6 (Upper). Disseminated ore. Dark and white areas are galena. Natural size.

FIG. 7 (Lower). Galena (dark and white areas) disseminated in dolomite. Note association of galena with stylolitic seam (nearly black surface at bottom). ×4/5.

Mode of Occurrence.

The mode of occurrence of the lead ores is the same for the entire district and, therefore, one description will serve for all the deposits without reference to particular localities. The writer's studies have been the most intensive in the Flat River-Rivermines area.

The ores occur in dolomite, in the order of importance, as follows: disseminated and bedded deposits, veins, and smaller cavity fillings. Only to a minor extent do any of the ores occur in the La Motte sandstones; those that do are disseminated and vein deposits and, rarely, bedded deposits. In the protore of the Washington County barite area, the galena occurs primarily in veins. All the chief modes of occurrence are associated, in some degree, in every ore body, and the one that predominates depends upon the character of the dolomite and its structural features.

Disseminated Deposits.—The galena is disseminated (Figs. 6, 7, and 8) through all the different phases of the dolomite. It replaces the dolomite, and occurs as both metasomes and metacrysts, which may be uniformly distributed through the rock, bunched within a bed, or aggregated along some structural feature, such as a joint or stylolite. The galena may be so abundant as to make up 75 per cent. of the rock, or so small in amount and so widely scattered as to be too lean to mine.

The metasomes range in size from mere powdery grains to those ⅜ inch in diameter (Figs. 6 and 7). They all tend to assume a cubical outline (they may acquire one or more faces) and, as a rule, are more or less intergrown with the dolomite. In fine- and medium-grained dolomite, the size of the metasomes is independent of the texture of the rock, but in a dense dolomite the galena is generally merely a fine powder or very small metasomes. Although the size of the metasomes (or metacrysts) is independent of the texture, the more coarsely crystalline phases of the dolomite are the more readily replaced, for reasons seen below. The metacrysts (Fig. 9) are dominantly cubes modified by octahedrons, but they may occur simply as cubes or octahedrons, or as octahedrons modified by cubes. They may attain

more than double the size of the metasomes, *i.e.*, 1 inch in diameter. The exterior of the crystals has a sheen, due to tiny pits which are the imprints of the dolomite grains against which the crystals were deposited. Not uncommonly, the metacrysts show

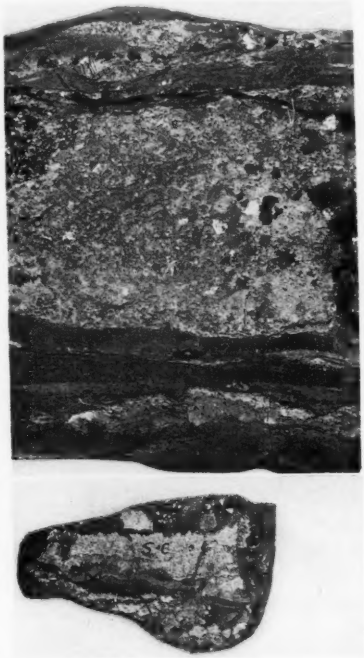


FIG. 8 (Upper). Galena replacing medium-grained glauconitic (small dark grains) dolomite. Siltstone layers at top and bottom. Slightly reduced.

FIG. 12 (Lower). Mammillary marcasite (*M*) and layer of siegenite-chalcopyrite (*S–C*) above. Slightly enlarged.

an internal radiating structure. Their distribution is similar to that of the metasomes.

The galena not only replaces the dolomite but any other constituent that may be present, such as quartz-sand grains, glau-

conite, oölites, or silt and shaly material. Replacement, however, does not always occur, as dolomite, quartz grains, glauconite, or any other material present in the dolomite may be included in the galena. The more porous layers (generally, the coarsely crystalline) are replaced most abundantly, and also contain larger metasomes and metacrysts. The color of the dolomite is unimportant in inducing replacement, although some men believe the contrary.

Bedded Deposits.—Bedded ores (Fig. 10) develop where the galena or marcasite replaces a particular bed of dolomite. Such solid beds of galena are, of course, very valuable ores. They may attain a thickness of 12 inches, but are mostly from 2 to 4 inches thick. They are generally persistent, attaining several hundred feet, but, they may also pinch out in a short distance. The bedded ores are not in all cases solid galena but (in beds containing from 25 to 50 per cent. galena) the galena may be so distributed as to have a bedded appearance. Marcasite is generally present. Even the practically solid galena beds may show unreplaced patches (islands) and streaks of dolomite. Just as in the disseminated deposits, all constituents of the dolomite may be replaced, or the grains of quartz (sand), dolomite, glauconite, or other materials may be residual in the galena. Even cavities (vugs) lined with crystals may occur in the bedded galena, showing that the dolomite was removed faster than galena was introduced.

The galena in these bedded ores is mostly coarsely crystalline (Fig. 10), but may be fine grained. It commonly shows curved cleavage faces. The same considerations of texture, porosity, and color hold for the bedded ores as were noted for the disseminated ores. The bedded ores are associated with an abundance of stylolites and stylolitic seams. They generally lie adjacent to the fairly thick (¼ to ½ inch) residual clay of the stylolitic seam.

Marcasite favors replacement deposits, either disseminated or bedded (Fig. 11). Bedded masses of marcasite, which may be three, four, or even more feet thick, occur in the mines, usually at the edge or top of a galena ore body. The marcasite com-

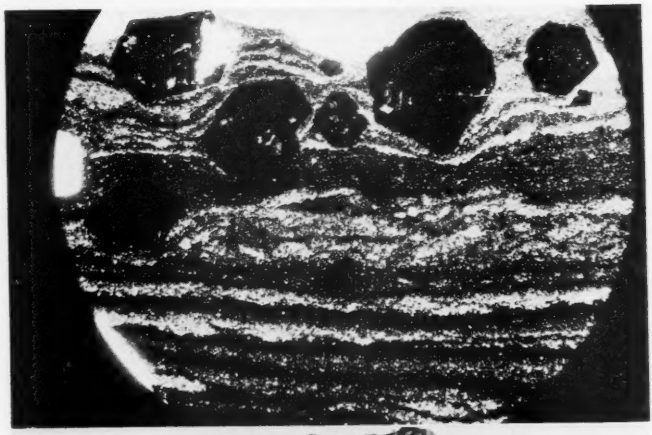


FIG. 9 (Upper). Metacrysts of galena in silty dolomite, and residual silty layers curving around the galena. 6×.

FIG. 10 (Lower). Solid bed of replacement ore, with coarse galena. ×4/5.

pletely replaces the dolomite and forms porous beds of stalactitic and colloform sulphide. The numerous vugs are lined with marcasite crystals. Galena may be sparingly present in these marcasite masses. The marcasite bodies show also some siegenite and chalcopyrite and, more rarely, sphalerite. At the Missouri Cobalt Mine, the siegenite and chalcopyrite occur in the great

FIG. 11. Marcasite (*M*) and galena (*G*) in specimen showing many stylolytic seams. Upper part shows small areas of residual dolomite surrounded by residual clays along solution planes. Narrow crooked band in lower part is calcite vein. Natural size.

marcasite masses that lie at the top of the La Motte sandstone and in the basal part of the Bonneterre dolomite. This sulphide ore body averaged from 2 to 4 feet in thickness, but in one place was, at least, 13 feet thick.

Veins.—Galena in veins is seldom regarded as a source of lead, but the writer believes that it is greater than is generally thought. In some stopes, especially in those in the upper parts of the mines, the veins are surprisingly numerous. The ore fragments in these

portions show the "glaze" lead (galena in thin sheets in the veins) on all sides. There are two types of vein deposits: filled fissures and replacement veins.

The filled veins (Fig. 13) are simply fissures (joints) in which the galena has been deposited, generally alone, but also with calcite, in places a little marcasite, and less commonly other sulphides, as noted below. Many of the vein walls show dolomite crystals with the galena deposited upon the crystals. For the most part, the veins are less than ⅛ inch in thickness, though, rarely, they may be nearly an inch. The galena occurs as crystals on the walls; and, as both large, thin crystals and a fine- or coarse-grained aggregate, it fills the fissures. Paper-thin veinlets extend out into the dolomite from the larger veins. The majority of these veins are not completely filled.

The replacement veins result where galena has replaced the walls of a joint or fissure. They are generally completely filled, and differ from the filled veins in the irregularity of outline of their walls and in being of more variable thickness. These veins are not so common as the filled type; in fact, they are more or less local. They were formed in fissures that were of insufficient size to take care of the mineralizing solutions.

The two types of veins are inclined; some are vertical. In dense and much shattered dolomite, inclined veins are the rule. Veins are not so common in porous beds, where disseminated ores prevail. If dense and porous layers alternate, the veins are in the dense layers. The veins, also, may contain siegenite and chalcopyrite associated with the galena, but this is not common. The siegenite and chalcopyrite may or may not have crystals forms. In a few veins that were evidently deposited during the closing stages of the mineralization, pyrite occurs along with calcite and galena.

Other Cavity Fillings.—These differ from veins in shape. Openings commonly utilized for deposition were the drusy cavities so abundant in many phases of the dolomite; as well as the larger irregular cavities, resulting apparently from solution. All of these openings are commonly lined with dolomite crystals upon

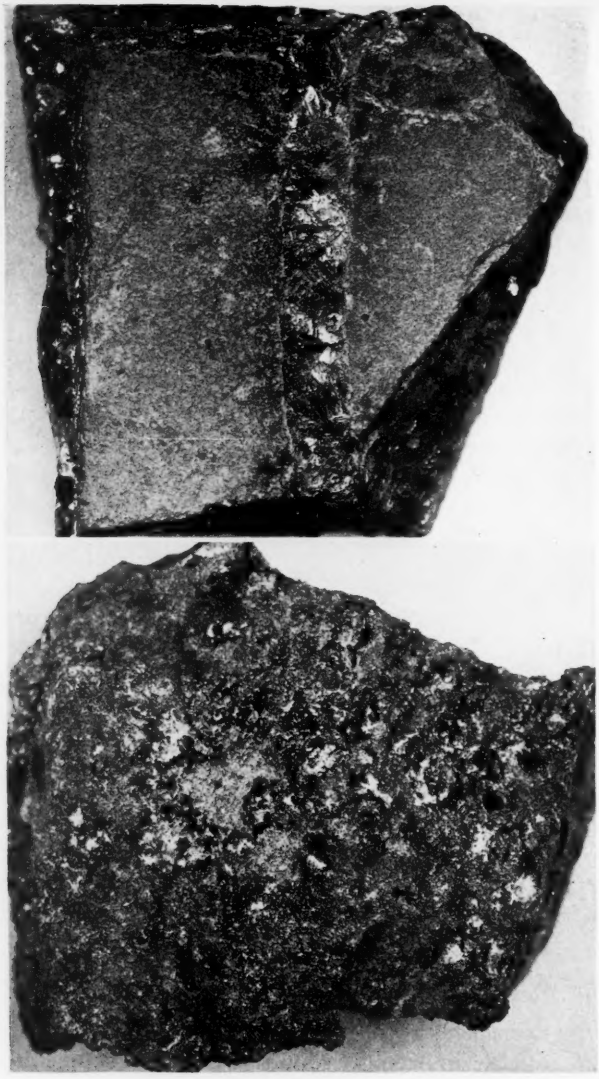


FIG. 13 (Upper). Filled-fissure vein. Another galena vein at left. Natural size.

FIG. 14 (Lower). Dickite (white) in cavities in marcasite. Small light-gray patches are dolomite containing marcasite. The cavities (black) in marcasite are lined with minute crystals of marcasite. Flat River mines. Natural size.

which the galena has been deposited. The galena occurs in crystals (either cubes modified by octahedrons or the reverse) and rarely, if ever, fills a cavity. The other sulphides are more commonly associated with the galena in these drusy cavities than

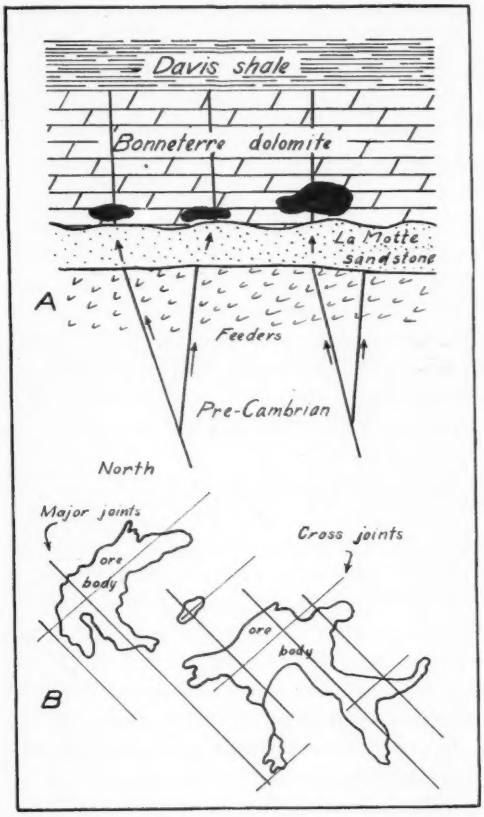


FIG. 15. Sketch *A* (section) shows how solutions rose from below along joints or faults (or both) and entered the La Motte sandstone, thence into Bonneterre dolomite. Sketch *B* (plan) illustrates dominant relationship of ore bodies to N.W.–S.E. joints, and the influence of joints nearly at right angles in spreading solutions laterally.

in the veins. The galena may replace the wall and extend out into the cavity. It is worth noting that, since these druses and other cavities commonly occur in porous layers, such cavity fillings are associated with disseminated ores, though less galena occurs in cavities than in disseminated form. Some of the larger solution cavities may be a foot or more across, and the minerals in them accurately show their *sequence of precipitation.*

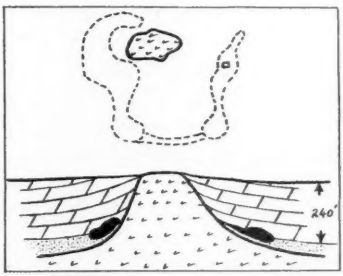
Position of the Ore Bodies.

The lead ores, as has been said, are in the Bonneterre dolomite. In the Flat River area, they may occur anywhere in the lower 270 feet (locally, they may be higher) of the formation (Fig. 15). Drill cores, however, show scattered galena to the top of the Bonneterre in various parts of the district, and the fact that galena occurred in the residual clays over the upper part of the dolomite is further testimony that the lead-bearing solutions reached to the top of the formation (and possibly higher), as they did in the Bonne Terre area. In the southeastern part of the district, galena was mined from residual clay along a water channel near the top of the Bonneterre.

In mine No. 10 of the St. Joseph Lead Company (in the southeast part of the district), the chief ore bodies lie between 100 and 270 feet above the base of the Bonneterre. They plunge southwestward about 1 foot in 500 feet, which is comparable to the dip of the Bonneterre. To the west and northwest of mine No. 10, the ore bodies steadily approach the base until, locally (*i.e.*, in Leadwood and in some of the mines below Flat River), they are at the very base of the dolomite. The ores at Bonne Terre have a vertical distribution of 200 feet. Pillars of ore of nearly this height may be seen in some of the stopes in both the Bonne Terre and Flat River districts.

The ores in Madison County all lie at the bottom of the Bonneterre and penetrate the sandstone. One ore body in the St. Joseph Lead Company's mine at Mine La Motte was entirely in the sandstone. The lead ore at the Missouri Cobalt Mine was at the base of the dolomite and just above the massive sulphide

ore that carried the copper, cobalt, and nickel. The ore bodies in this mine occur in a trap surrounding a small knob of granite porphyry (locally a fine-grained granite). The major ore body occurs on the east and south sides, although ore was said to occur all around the knob. The mineralization occurs in the granite porphyry, as well as in the sandstone and dolomite. It can hardly be doubted that other occurrences of ore also owe their localization to buried hills of granite or porphyry, although the hills may not have been encountered during mining operations. Porphyry



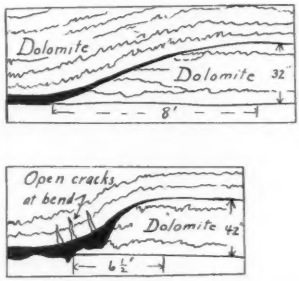


FIG. 16 (Left). Sketch showing mode of occurrence of ores (black areas) around buried granite-porphyry hill at Missouri Cobalt Mine. Dotted lines indicate ore bodies in plan.

FIG. 17 (Right). Sketches showing how rich beds of ore (black) were formed by removal of 32 and 42 inches of dolomite. Note abruptness of change, and letting down of upper beds. Mine No. 16, St. Joseph Lead Co.

hills have been found in the mines of the Leadwood and Bonne Terre areas, and the undulating upper surface of the La Motte sandstone doubtless suggests other buried hills.

The ore bodies, in general, are horizontal and follow a given series of beds fairly persistently, though they may occur also in beds higher or lower than the main series. There are many stopes in which the ores are distributed vertically through 200 feet. The ore is not uniform in tenor throughout this height (some parts being too lean to mine) but the mixture of high- and

low-grade ore meets the minimum standard for the mills. Some individual ore bodies of very excellent tenor average 10–15 feet in thickness for more than 1,000 feet and have a variable width of 200–300 feet. The ore bodies of the lower horizon may be from 10–50 feet thick and are, in general, more persistent than those in the upper horizon. These upper ores range from a few feet to 200 feet in thickness, and are more variable in tenor.

The horizontal distribution of the ores is variable (Fig. 15). Mining may stop because the ore becomes too low in grade or because the ore body stops. Excellent ore may cease within the space of a few inches. A drift in one mine missed a rich ore body (found later) by between 18 and 24 inches. Even within an ore body, the tenor may vary with extreme rapidity. Drills have penetrated nearly barren dolomite in the midst of an excellent ore body. It was noted that certain persistent ore bodies, for example, those in stope 4,587 (Fig. 18) and other stopes in mine No. 16, end rather abruptly (within 6 to 100 feet). The beds beyond become thicker and barren (Figs. 17 and 18). The

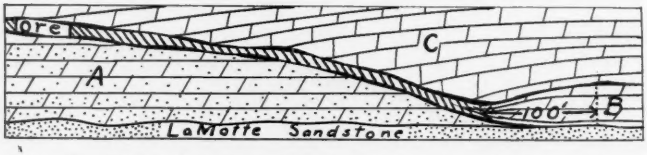


FIG. 18. Sketch showing concentration of ore by solution of dolomite. Ore ends against essentially barren dolomite (*B*). Dolomites *C* and *A* have been removed along the ore bed. Mine No. 16, St. Joseph Lead Co.

significance of this will be noted below under the discussion of concentration. The companies use diamond drills in thoroughly prospecting their properties and in determining the presence and size of an ore body. A study of the mine maps showing the ore bodies in plan reveals little evidence of a definite alignment or relationship to any structural element. The major evidence in the Flat River-Leadwood area suggests a northeast-southwest trend about parallel to that of the major joints and channels, *i.e.*, N. 80° E.

The ore is richer adjacent to the water channels or major joints, but not all ores are directly associated with them. Strong joints occur in most of the stopes (as well as in the barren rock outside), although they may not be water channels at present. The walls of many of these joints show evidence of oxidation by surface waters, even though the joints contain little water. There is no doubt but that the large joints have a direct relationship to the ore bodies, nor that this relationship is supplemented by the smaller joints.

No positive evidence is available that certain portions of the Bonneterre dolomite are more suitable for ore deposition than others. The formation is remarkably uniform from bottom to top. Its chief variations are in its glauconite content and in its color, texture, and porosity. The glauconite has no relationship to the deposition of the ores, and since ores occur in dolomite of every shade of color in various portions of the mines the color can scarcely be regarded as of significance. The texture and porosity of the rock have certainly influenced its permeability to solutions, and subsequent deposition, but as the ores are not confined to the parts of the rock having a similar texture and porosity, these features cannot be determining factors in the deposition of the ores. The influence of the shale (and dark color) was strongly emphasized by Buckley, as well as others, but the writer's studies have shown that shales are very minor and unimportant constituents of the formation, the supposed "shales" being dominantly residual clays resulting from the solution work to which the dolomite has been subjected. Most of the ores are associated with portions of the dolomite that are rich in these solution effects (stylolites, stylolitic seams, and other solution planes), as will be explained below. The dolomite and any of its constituents were readily replaceable by the ore solutions, the composition having little influence upon this replacement though the porosity and texture of the rock did.

Faults cut the ore bodies in all of the mines. In some, they have displaced the ore body 30, 40, or (rarely) 100 feet, necessitating mining on different levels. Most of the faults, however,

are small, having only a few feet (some, only inches) of displacement. The same horizon carries the ore on both sides of the fault. No faults seen by the writer show positive evidence of mineralization or indication of their having acted as ore-bearing channels, though it has been stated that there was such evidence.

That some of the faulting is undoubtedly post-mineralization in age is positively proved by the abundance of crushed galena present in the slickensided gouge of an important step fault (total displacement about 20 feet) that cuts the lower ore body in stope 18,330 of the St. Joseph Lead Company's mine No. 1. Not only was the finely crushed galena present along the slickensides, but large grains of galena were elongated, as shown by distorted faces, curved cleavage faces, and internal slip planes paralleling the direction of movement. Small cubes were distorted into rhombic forms which depart as much as 17° from a right angle; octahedrons were elongated parallel to the movement. Glauconite grains were crushed and ground up with the dolomite, clay, and silt, which constitute the remainder of the gouge. Similar positive evidence was found in other faults, and could, no doubt, be duplicated in many more.

Some observers have suggested that the faults are pre-mineralization in age, and that the solutions were selective, always replacing the same horizon on both sides of the fault whenever they reached it. The fact that the faults themselves are barren of ore (except the crushed material) throughout the lead district is absolutely opposed to this idea, but of equal significance is the fact that the ore body does not always follow the same horizon but may be found above or below in another horizon which had also been cut by the fault, but not "selected" for general mineralization. Furthermore, the great vertical range of 300 feet of mineralization, even though the tenor of the ores is variable, indicates that selectivity was not an important factor in the deposition of the ores. The abrupt lateral termination of the ores (even though the bed that contained them continues) is also opposed to this view. Lastly, the best ores are associated with major joints that show no evidence of movement, a relationship that is undoubtedly genetic.

Mineralogy of the Ores.

The mineralogy of the lead ores is simple. Galena is the only important lead mineral, though cerussite may be present near the surface. The associated sulphide minerals are marcasite, chalcopyrite, siegenite, sphalerite, and pyrite. The other gangue minerals are dolomite (both as the rock and the mineral), calcite, glauconite, quartz (as sand grains and crystals), clay minerals, and last, but very important, dickite. Where oxidizing solutions have reached the ores, there have been formed (in addition to cerussite) melaconite and brochantite (from chalcopyrite); bieberite, asbolite, and morenosite (from the siegenite); and the inevitable iron oxides.

Galena.—The galena occurs as crystals and anhedral grains. The crystals normally possess a cubic form modified by an octahedron, but octahedrons modified by cubes also occur. The former predominate as metacrysts and in veins, and the latter are more common in cavities. A group of tiny radiating rods (maximum length ⅜ inch) of galena was found in one cavity. They were elongated cubes. The galena may show an internal radial structure. The surface of the crystals is smooth, curved, or pitted from incomplete growth. Some crystals are composed of curved plates which, if thin, give the surface a feathery appearance. The crystals in cavities and veins show casts of the dolomite or marcasite crystals on which the galena was deposited. The metacrysts may be rough on the surface, showing the contact with the dolomite, or they may possess a sheen if the contact was with very fine dolomite. The crystals normally range from an inch across down to microscopic sizes. Rarely, crystals five inches across have been found.

The anhedral forms are especially abundant in the bedded, disseminated, and filled-vein deposits. Their internal structure is always crystalline, and so strong is the cubic crystallizing force that even these forms, especially metasomes, tend to have a cubic outline. Metasomes rarely exceed ⅜ inch in diameter, but anhedral forms in the massive ores may be an inch across. From this size, they range down to that of a fine powder. All forms

of galena may contain unreplaced dolomite, glauconite, sand grains, and sulphides.

Marcasite.—Marcasite (called "pyrite" in most of the previous reports on the district) ranks next to galena in abundance. It occurs as well developed crystals, and as anhedral grains and aggregates. Radial or fibrous forms are rare. Few of the crystals exceed 3/8 inch in length. Simple crystals showing the prism *m*, the basal pinacoid *c*, and the striated faces on the brachydome are abundant. Another less common single crystal has the basal pinacoid well developed, which reduces the area of the brachydomes. Twins (with *m* as the twinning plane) giving rise to arrow-shaped forms with the striated brachydome faces meeting at the twinning plane are also common. All these crystal forms occur abundantly in the disseminated and bedded ores and in the cavities. The crystallization power of marcasite during replacement appears to exceed even that of galena, as metacrysts are more abundant than metasomes. It should be noted that marcasite is least abundant in the veins. It is very abundant in the stylolitic portions of the ores, where it may be very fine-grained and extend into the adjacent dolomite from the stylolite or seam. Stalactitic and mammillary (Fig. 12) forms of marcasite alternating with pyrite were observed in the Missouri Cobalt Mine, and colloform aggregates of marcasite, pyrite, and possibly melnikovite [10] occur about three miles from this mine.

Siegenite.—Siegenite,[11] (Ni Co Cu Fe) (Ni Co Fe)$_2$ S$_4$ (a mineral containing Co–Ni in nearly equal amounts), has been called "linnæite" in previous reports of this district. It is a silvery-white mineral with a pink tint. This color and the very common octahedral (modified by the cube) habit of siegenite make identification easy. Twins are common. Siegenite occurs both as metacrysts and metasomes, but the former are much the more common; in fact, as with marcasite, metacrysts of siegenite are relatively more common than metacrysts of galena. Crystals

[10] Tarr, W. A.: Alternating Deposition of Pyrite, Marcasite and possibly Melnikovite. Am. Min., vol. 12, p. 417, 1927.

[11] Tarr, W. A.: The Linnæite Group of Cobalt-Nickel-Iron-Copper Sulfides. Am. Min., vol. 20, pp. 69–80, 1935.

with diameters of ⅜ inch (1 cm.) across are not uncommon. The siegenite may replace entirely all other minerals (dolomite, glauconite, sand grains, and rarely marcasite), or it may contain all of these (as well as charcopyrite) as inclusions. The siegenite may be intergrown with the chalcopyrite, indicating simultaneous deposition, or it may be replaced by it. Siegenite is to be found in small amounts in all parts of the mines in the lead belt. It is also found in cores from diamond drills. It is most abundant at the Missouri Cobalt Mine (where it was the source of the cobalt and nickel in the ore) and Mine La Motte. Its composition at the latter locality, as determined by Henry Lix [12] in 1932, is as follows: S, 42.43 per cent.; Co, 20.36 per cent.; Ni, 31.24 per cent.; Fe, 3.22 per cent.; Cu 3.16 per cent.; total, 100.31 per cent.

Chalcopyrite.—Chalcopyrite is a common, but not invariable, associate of siegenite. Each mineral may occur alone, even though only inches apart; or they may be intimately associated, either intergrown or the chalcopyrite may replace the siegenite. Chalcopyrite may occur unassociated with any other sulphide, and, locally, may be so abundant (as in one stope at Mine La Motte) as to constitute a copper ore. It rarely occurs in crystals (save in occasional cavities) and is generally massive. The crystals are the usual distorted sphenoids. Chalcopyrite may replace the dolomite, marcasite, or siegenite, or be deposited in cavities. At Mine La Motte, some chalcopyrite replaces galena.

Sphalerite.—Sphalerite is a rare constituent of the ores, but it is probably more common than is supposed for zinc always appears among the by-product metals recovered during smelting. In the Leadwood mines, some drill cores showed from 3 to 5 per cent. of zinc ore and one showed two feet of 11 per cent. ore; it is also abundant in the Missouri cobalt ores. The sphalerite is generally dark colored and hence is easily overlooked among the other ore minerals, but that at the Missouri Cobalt Mine is mostly lighter in color. The sphalerite ranges from fine-grained to coarsely crystalline material. Rarely, it occurs as imperfect

[12] Lix, Henry, University of Missouri Thesis, 1932.

metacrysts, but usually as metasomes replacing all other materials. It is, therefore, most common in the ores formed by replacement.

Pyrite.—Pyrite is surprisingly scarce in the ores. It occurs along with calcite and some galena, generally as very small cubes in the veins. Rare crystals of pyrite an inch in diameter occur in some of the large solution cavities or well marked veins. A few small octahedrons, modified by cubes, were observed in a thin veinlet. No pyrite was proved to be present in the disseminated or bedded ores. It is apparently confined to the closing stages of mineral deposition, as the veins that contain it were the latest formed.

Dolomite.—Dolomite is present both as the rock and the mineral. As the rock, it constitutes the country rock of the ores (save for the small amount of ore in the La Motte sandstone), hence is a major constituent of all ores. The mineral dolomite occurs as perfectly formed crystals (rarely exceeding ⅛ inch across) lining druses, solution cavities, joints, and ore veins. These crystals are mostly on the walls of the openings, but rarely a later generation of crystals is deposited on the sulphides. The rhombohedral crystals are white or transparent, and may show phantom crystals. They apparently contain less iron carbonate than does the rock dolomite, for the color change of the mineral on exposure to the air is much slower than that of the rock, which assumes a rusty color after a few weeks' exposure on the dumps.

Calcite.—Calcite is common in veins and solution cavities throughout the mines. One set of calcite veins is entirely free from galena, but another set shows galena and other sulphides. In the majority of calcite-bearing veins, the calcite is the last mineral deposited, though in some earlier veins galena and marcasite have replaced the calcite. Some large masses of calcite are associated with the water channels that show oxidation. As $CaCO_3$ is being deposited from some of these waters at present, the calcite is also related to them. Most of the calcite is white. It is mostly in coarsely crystalline masses, but crystals up to several inches in diameter occur in some large cavities. The calcite veins tend to parallel the good ore bodies, but also follow other courses.

Glauconite.—Glauconite is a primary constituent of the dolomite and has been described above. It is most abundant in the lower 100-feet of the Bonneterre. It may be replaced by the sulphides or included in them.

Quartz.—Quartz occurs in two forms in the ores; one as sand grains, and the other as minute, doubly terminated, transparent crystals. The sand grains form the sandy phases of the lower Bonneterre dolomite. The minute quartz crystals occur on dolomite crystals or marcasite in druses and veins. They are abundant in the Annapolis deposits.

Clay Minerals.—Clay minerals make up the shale layers and the clay-like residual material along the stylolites and other solution planes. It is of interest to note that some of this residual material has optical properties strongly suggestive of biedellite. A small quantity of kaolinite was noted in altered feldspar phenocrysts of porphyry pebbles in the conglomerate bed.

Dickite.—The most outstanding discovery in the study of the ores was the finding of dickite, a hydrothermal member of the clay minerals. The dickite was first recognized in a specimen of marcasite from one of the St. Joseph Lead Company's mines about three miles southeast of Flat River. The determination of the optical properties and the results of an X-ray examination left no doubt but that the mineral was dickite. As dickite has been shown to be of hydrothermal origin (it occurs abundantly with the cinnabar in Pike County, Arkansas, for example), its occurrence with the lead ores is of especial significance. The dickite occurs in snow-white scales, biaxial positive, index 1.562–3, extinction 10° +. It is found in cavities in marcasite (Fig. 14) and dolomite. Galena also occurs in these cavities, but the dickite is later than the galena. The dickite may fill a cavity or only the *lower part;* calcite may occur in the upper part. Its mode of occurrence shows that in crystallizing from solutions it settled downward in the cavities. As dickite was found to be abundant in this part of the district, it becomes an important diagnostic constituent bearing upon the origin of the ores.

Cerussite.—Cerussite in the form of small crystals was noted in a few specimens found near the water courses. It invariably occurs on the galena and, as other carbonates are abundant among the ores, its origin is easily understood. About sixteen years ago when attempts to mine and mill the residual clay (as well as underlying Bonneterre at Mine La Motte) were being made, it was found that a notable quantity (estimated at 8 per cent.) of lead carbonate as small grains was present in the residual clays. Radiating aggregates of cerussite crystals (maximum length, 1½ inches) occurred with the lead ores at Mine La Motte. They were in any of the numerous cavities in the dolomite and most abundant just below the residual clay.

Copper Minerals.—Brochantite, a basic sulphate of copper; malachite, the carbonate; and melaconite (CuO) are oxidized copper minerals that have been noted in association with the chalcopyrite, but all are extremely rare.

Cobalt Minerals.—Three rare cobalt minerals occur at Mine La Motte: asbolite (cobalt wad); bieberite, $CoSO_4 \cdot 7H_2O$; and morenosite, $NiSO_4 \cdot 7H_2O$. The asbolite is found on outcrops of the siegenite-bearing La Motte sandstone. The asbolite contains copper, as well as cobalt oxide, and is an amorphous, hard, black mineral. The pink bieberite and green morenosite are common as efflorescences on the pillars (of siegenite-bearing sandstone) in the mines. The bieberite is the more abundant.

Iron Minerals.—The ubiquitous iron oxides were noted in the channels of active water circulation, as well as in the dolomite adjacent to them.

Paragenesis.

The sequence of deposition of the various minerals of an ore body is of the utmost value in interpreting their depositional history. For the most part, in the Missouri lead ores, there is evidence of a relatively simple sequence, but departures occur that involve overlap, repeated deposition, and replacement. Although, in the main, the sequence is the same throughout the district, there are variations in the different modes of occurrence.

The normal sequence in most of the replacement ores in the dolomite (or sandstone) is (1) marcasite, (2) galena. Where the minor sulphides are present the sequence is as follows:

The following sequences, after galena, were noted and others probably exist. These sequences were not common.

1	2	3
Dickite	Marcasite or pyrite	Dolomite crystals
	Pyrite or marcasite	Dickite
	Quartz crystals	
	Dolomite crystals	
	Dickite	
	Calcite	

Where overlap occurs the sequence is normally as follows:

The following minerals were found replacing one another sequentially: marcasite, siegenite, chalcopyrite, sphalerite, galena. The marcasite was almost invariably the first sulphide deposited; rarely, it is recurrent and follows the other metallic sulphides. Where marcasite and galena occur alone, the marcasite precedes the galena. The galena may penetrate the dolomite beyond the marcasite, which is mostly deposited near the feeding joint. The marcasite will cling to a stylolite seam (mode of ingress), whereas the galena is found out in the dolomite as a replacement, or in a cavity. The galena is consistently coarser than the marcasite and there is little or no evidence that it has ever replaced the marcasite.

The two minerals may be in contact, but a surprising feature

is their independence of each other. This suggests a time difference in deposition and a different physio-chemical set up. The large masses of marcasite ore were doubtless deposited rapidly. Their position relative to the source channels probably represents the maximum penetration by solutions at the time of the greatest temperature and acidity, hence the occurrence of these masses at the outer edge of certain ore bodies (a feature noted by the miners and interpreted by them as indicating the edge of the ore body). However, another interpretation is possible. Since there is little intimate association of the two sulphides, a considerable time interval may have existed between their depositional periods, the deposition of galena occurring later than that of the marcasite. A marked variation in the physio-chemical character of the solutions could then have occurred.

Where the cobalt-nickel-copper (and, less commonly, zinc) sulphides appear in the ores, they follow the marcasite and precede the galena. The siegenite follows the marcasite, as a rule, and probably replaces it, but no positive proof of this was found. No overlap was noted, but it doubtless occurred, especially in the replacement deposits. Siegenite may occur without marcasite. The chalcopyrite commonly overlaps with the siegenite and also replaces it. If the siegenite is missing, the chalcopyrite is deposited on the marcasite; or, if the siegenite is later than the chalcopyrite (an unusual order), the chalcopyrite may be deposited on the marcasite. The sphalerite follows the other sulphides, which it may replace; or, the order may be reversed, and the sphalerite follow even the galena. The occurrence of sphalerite is so rare as to make it difficult to decide positively about the sequence.

Galena is consistently last, especially in the ores. In veins and cavities, it may be followed by any of the preceding sulphides, but such recurrences are rare and are apparently due to an influx of new solutions. The galena may replace any of the other sulphides, as well as the dolomite and, less commonly, the silty and shaly bands.

All of the sulphides seemingly favor an independent occurrence,

since one side of a specimen, one inch thick, may show siegenite with no other sulphides, and the other side, only chalcopyrite. In the disseminated and bedded ores if all of the minerals occur, overlap and replacement are common, but in the veins and cavities a longer time break is evident since excellent crystals are deposited one upon the other. Dolomite crystals normally occur on the walls of veins, druses, and other cavities, and a second generation may appear after the sulphides were deposited. Pyrite may alternate in sequence with the second generation of dolomite crystals. Quartz follows the dolomite or pyrite. Dickite follows the galena but may be later than the dolomite, pyrite, and quartz. Its relationship to calcite is unknown. Calcite is generally last unless it belongs to one of the earlier vein systems.

In the replacement deposits, the mineral sequence indicates an initial period of marcasite deposition (in good crystals) which was relatively slow as essentially all the marcasite is crystalline. When the solutions contained small amounts of cobalt-nickel, the deposition of siegenite may have begun before that of marcasite had ceased; or, if later, it replaced the marcasite. Chalcopyrite commonly overlaps the siegenite; if later, replacement occurred, or the chalcopyrite was deposited on the siegenite. There was evidently a time break before the zinc came down as sphalerite, which replaced the dolomite or any other mineral. The quantity of these cobalt-nickel-copper-zinc minerals was always small (except at the Missouri Cobalt Mine and Mine La Motte), hence in most of the ores they are absent and the next mineral deposited after marcasite was galena. The galena consistently follows the marcasite (or other sulphides). It replaces the dolomite and molds itself about the marcasite and other sulphides, but only rarely replaces them.

The sequence in filled veins and other cavities is essentially the same as in replacement ores, save that dolomite crystals may be deposited on the walls, first, followed by the sulphides. The minerals deposited in these open spaces have better crystal forms. Overlap and replacement are less common. Dolomite and, rarely,

pyrite and quartz crystals appear after the galena. The dickite follows the galena and is later than the other minerals. Calcite was the last of the minerals to be deposited in the ores, but it was also deposited in pre-sulphide time because in some veins the other minerals have replaced it.

The above sequence is apparently the normal one for each type of deposit in the entire district, but evidence was found that certain minerals (marcasite, siegenite, chalcopyrite, sphalerite, and pyrite), in small amounts, appear after galena. In a few specimens, chalcopyrite and pyrite appeared both before and after galena. Such recurrences and subsequent deposition were evidently due to a resurgence of the mineralizing solutions. The solutions were not active, chemically, as is shown primarily by the deposition in cavities and open spaces. One vein showed evidence of having been reopened.

The normal paragenesis for the district shows that the major deposition of ore minerals was confined to one general period. The occurrence of cobalt, nickel, copper, and zinc minerals with the lead ores throughout the district (in small amounts in the lead belt proper and abundantly near Fredericktown) leaves no doubt but that all the metals came from a common source.

(*To be concluded in next number.*)

UNIVERSITY OF MISSOURI,
COLUMBIA, MO.,
Aug., 1936.

THE OCCURRENCE OF LAKE BOTTOM MANGANIFEROUS DEPOSITS IN CANADIAN LAKES.[1]

E. M. KINDLE.

INTRODUCTION.

It is the purpose of this paper to record information now available concerning the distribution and manner of occurrence of manganiferous concretions and other manganese oxide deposits that develop on certain lake bottoms. Field studies made since the publication of two earlier papers by the writer [2] on manganiferous concretions in 1932 and 1935 have considerably extended the known distribution of these deposits.

During the summer of 1935 several days were devoted to a study of this type of lake bottom deposit in various parts of Nova Scotia. In this field work Dr. C. H. Kindle gave valuable assistance. Lake studies in Ontario have extended the known distribution from lakes on or near the Atlantic coast to lakes in southern Ontario. During the writer's first work on lacustrine manganiferous deposits the concretions of manganese oxide which were found were almost entirely limited to the relatively shallow parts of the lakes examined. Other lakes are now known where the manganese oxide appears to occur only in the maximum depths.

OCCURRENCE IN NOVA SCOTIA LAKES.

The manganiferous concretions that are present in certain localities in the shallow marginal waters of various Nova Scotia lakes have already been described and figured.[3] These structures which

[1] Published with the permission of the Director, Bureau of Economic Geology, Department of Mines, Ottawa.

[2] Kindle, E. M.: Lacustrine Concretions of Manganese. Am. Jour. Sci., vol. 24, pp. 496–504, 1932.

[3] Kindle, E. M.: Manganese Concretions in Nova Scotia Lakes. Roy. Soc. Can. Trans. Sect. IV, pp. 163–180, 1935.

have been developed in water from a few inches to a few feet in depth and subjected to wave action have a distinctly different surface from the types formed in depths and locations where they escape the environment of breaking waves. An example of the

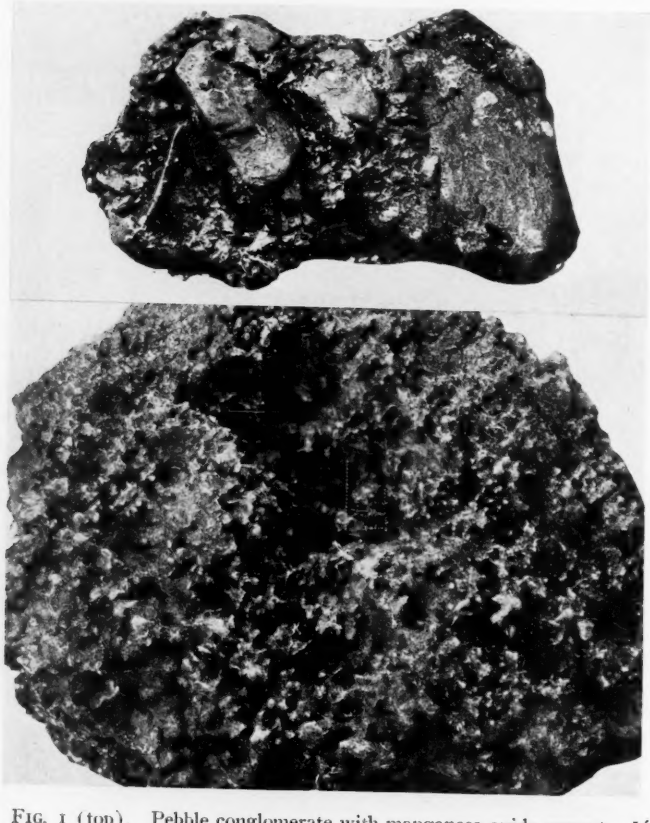


FIG. 1 (top). Pebble conglomerate with manganese oxide cement. ¼ nat. size. Kedgemakooge Lake, N. S.

FIG. 2 (bottom). Manganese oxide deposit on flat pebble showing delicate spicules developed in water about 20 feet deep. Head of river outlet, Ship Harbour Lake, N. S. 4/5 nat. size.

latter type was taken from a depth of about 20 feet at the head of the outlet river from Ship Harbour Lake. The deeper water structures show a highly irregular surface studded with spicules of manganese oxide (Fig. 2). This type of surface is in sharp contrast with the rugose but comparatively regular surface of the shoal water concretions.

Another type of the manganese oxide deposit is associated with marginal lake waters where in place of a sand, gravel, or small boulder and gravel beach, angular blocks and slabs of rocks of various sizes encumber the shallow near shore lake bottom. In such lakes with favorable conditions for manganese oxide deposition the entire surface of every rock slab or boulder may be covered with a thin coating of manganese oxide from ⅛ to 1 inch thick which has always a very rough surface. Such deposits commonly cover the entire surface of every rock fragment and boulder on the bottom, cementing all of the boulders and slabs at their points of contact into a solid mass from which it is difficult to separate even a small boulder without the use of a crowbar. A good example of this type of deposit occurs in a lake 16½ miles northwest of Sheet Harbour, N. S., on the southwest side of the highway (Fig. 3).

Another type of deposit forms a firm black conglomerate. The manganese oxide in shallow parts of the lake accumulates as a blanket deposit on all of the gravel boulders and angular pieces of rock, converting them into a continuous thin sheet of conglomerate (Fig. 1).

A good example of the manganese oxide conglomerate deposit was found in Christopher Lake No. 2, S.E. of Caledonia N. S. 4½ miles. A belt of coarse gravel and small boulders firmly cemented by manganese oxide forms a nearly continuous belt a few yards wide in water 1 to 4 feet deep along the south shore of this lake. From a depth of 4 feet the water deepens rather abruptly to 8 or 10 feet and a bottom of dark brownish mud replaces the cemented pebble and boulder near shore belt. In this and other Nova Scotia lakes the manganese oxide deposit is unknown on the soft mud bottom zone.

The manganese conglomerate is well developed 8 miles west of Caledonia along the northeast shore of Lake Kedgemakooge—the only part of the lake examined. It may be seen there opposite Murray's Camps around a gravel and boulder island. A feature of interest in the Kedgemakooge Lake shore is the presence of narrow inlets or shore indentations. The heavy manganese oxide coating on all the gravel and boulder bottom near shore stops abruptly at the entrance to these small coves some of which have lillies about the cove heads. The point at which the manganese

FIG. 3. Deposit of manganese oxide on rock slab from water about 20 inches deep. Lake 16½ miles northwest of Sheet Harbour ½ nat. size.

deposit stops coincides with the locus of contact of agitated and quiet water in breezy weather. Only very slightly coated rocks are found where wave action is slight and none where it is entirely lacking. The conclusion seems unavoidable that the increased facility for oxidation of the manganese in the water afforded by localities favorable to wave action is an important factor in the development of the manganiferous deposits.

The geographical distribution of the manganiferous concretions, and cemented pebble and boulder deposits is now known to

have a northeast by southwest extent of 140 miles, from the vicinity of Sheet Harbour in northeastern Nova Scotia to Kedgemakooge Lake in Queens and Annapolis Counties in the southwestern part of the province. All of the lakes in which these deposits are known to be well developed in Nova Scotia lie within the region of the Gold-bearing series of rocks and fall in the class of soft water lakes. The widespread occurrence of lakes throughout the area underlaid by this rock series which have been found to be depositing manganese oxide, makes it most probable that the occurrence of such lakes is coextensive with the distribution of the Gold-bearing rock series or from Cape Canso to Yarmouth.

ONTARIO LAKES.

Bottom samples taken in Loughborough Lake eight miles northwest of Kingston, Ont., in 1934 disclosed the presence of manganese oxide in the deepest part of this lake.[4] This discovery of manganese oxide was made in a hard water lake after collecting manganese concretions from various Nova Scotia lakes all of which were soft water lakes. It demonstrates that manganese and iron oxide deposits occur in lake bottoms regardless of the abundance or scarcity of lime in the water.

The bathymetric occurrence of manganese oxide in Loughborough Lake however is limited to the deepest part of the lake whereas in the Nova Scotia lakes it is most abundant in the shallow waters. The upper four miles of Loughborough Lake is a limestone basin and considerable stretches of the near shore waters on the southeast side are floored with white marl. An example of the soft black somewhat sandy manganiferous material taken from a depth of 105 feet was made by Mr. R. J. C. Fabry and shows the following constituents: SiO_2, 27.51; Al_2O_3, 5.14; Fe_2O_3, 13.19; FeO, 1.14; CaO, 5.10; MgO, 1.31; H_2O, 10.80; MnO_2, 32.66; CO_2, 2.17; total, 99.02.

The unique occurrence of this manganiferous deposit in the deepest part of the lake led the writer to resample the section a year after the original visit in the hope of finding the manganese-

[4] This work was financed by a small grant from the Sedimentation Committee of the U. S. National Research Council.

iron oxide sediment elsewhere on the lake bottom. The details of the samples from 1000 feet of the western end of the bottom section studied between Cedar Grove and the mouth of a small brook one mile northeast of the head of the lake are as follows:

LAKE BOTTOM SECTION.

Station	1	from	W.	shore	120′	Depth 62′	Coarse gravel.
"	2	"	W.	"	200′	" 84′	Blue grey clay.
"	3	"	W.	"	300′	" 105′	Coarse gravel sand and small bits of black sediment (MnO_2).
"	4	"	W.	"	400′	" 90′	Black ooze.
"	5	"	W.	"	500′	" 92′	Black ooze and mud.
"	6	"	W.	"	700′	" 90′	Greyish to black soft mud.
"	7	"	W.	"	1000′	" 90′	Same as Sta. 6.

Eastward from station 7 the lake shoals gradually, and hard clay appears in some samples before reaching the marl belt near the east shore. Each of the two traverses that have been run across the lake from Cedar Grove have located the soft black mineral found at station 3 in the deep water zone about 300 feet from shore but nowhere else (Fig. 4).

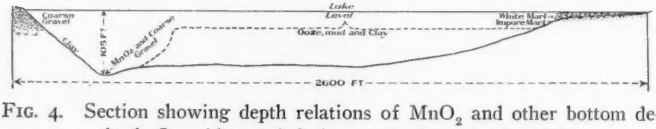


FIG. 4. Section showing depth relations of MnO_2 and other bottom deposits in Loughborough Lake, 1 mile from head of lake.

The white marl with which the section ends on the east side terminates lakewards with a cornice-like margin beyond which the lake deepens rather abruptly from 4 or 5 feet to 10 or 12 feet.

Examples of manganiferous concretions have been brought to the writer's notice by Mr. A. La Rocque which were brought up on trout lines from the deeper waters of Big Trout Lake and Cedar Lake in Algonquin Park, Ontario. Future discoveries may be expected to extend the known distribution of manganiferous sediments beyond the limits of the three Ontario lakes now known to contain these sediments.

GEOLOGICAL SURVEY OF CANADA,
OTTAWA, CANADA,
August 3, 1936.

COLLOIDAL TIN ORE DEPOSITS.

ROBERT HERZENBERG.

PEGMATITIC pneumatolytic processes and also high temperature hydrothermal processes cannot entirely account for the features observed in some of the tin deposits of Bolivia, especially in the districts of Oruro and Potosi. Such processes do not account for the fact that the cassiterite was formed at very low temperatures, that it was formed at every stage of the ore deposition, and that in places it was the latest mineral formed, even later than kaolin, alunite, and siderite. Neither do they explain the colloform structure of wood tin nor the extremely fine grains of tin minerals, which makes the beneficiation of Bolivian tin ores such a difficult task. For example, tailings from tin ores contain up to 2 per cent of tin and extraction from low grade ores is only about 20 per cent.[1] Further, such processes do not explain the extreme irregularity of the distribution of the ore shoots and the variability of the tin content, since along with rich parts (guias) low grade ores are also found. Finally such processes do not account for the local enrichments of tin within the mines.

The basis of the pneumatolytic theory was the classical experiments of Daubrée,[2] who showed that tin fluoride reacted with steam, yielding crystals of cassiterite, and that the liberated hydrofluoric acid resulted in the formation of fluorine-bearing minerals such as fluorite, topaz, and apatite. The scarcity of these minerals in the tin deposits of Oruro and Potosi has led to the belief that in Bolivia the pneumatolytic action was accompanied by boron and not by fluorine because of the commonness of tourmaline. However, the theory of boron pneumatolytic action lacks experimental evidence. Neither the borite of tin nor

[1] One tin mine in Negro Pabellon near Oruro has a chalky-like ore containing about 50 per cent tin, but every attempt to concentrate it has failed.

[2] Daubrée, A.: Annal. d. Mines, 4th ser., vol. 16, p. 29, 1849.

its reactions are known. It is assumed that the borite of tin would be a carbide-like substance—hard with a high fusing point and only slightly volatile. No boron-bearing tin minerals have been reported from Bolivia, also there is no established functional connection between the tin deposits and the tourmalinisation. Tourmaline rocks occur without tin, and tin without tourmaline. The coincidence must be only casual.

Ahlfeld[3] supposes that deep-seated hydrothermal solutions have transported the cassiterite upward:

> Through deep fractures formed after the intrusion of batholiths and of near-surface masses, the solutions accumulated under high pressure were suddenly ejected to near the surface, and there, under rapidly decreasing temperature and pressure, instantly yielded their metallic content. Therefore, tin had no opportunity to precipitate completely from the solutions at high temperatures near the batholiths, but remained in part in solutions in labile equilibrium. The components that originally existed as ions in solution went through a phase of sols and precipitated as mixed colloids which later unmixed and crystallized.

Ahlfeld's conception is not quite clear to me. If the solutions instantly yielded their metallic content, what is there to remain in solution in labile equilibrium? The zonal structure of most cassiterite crystals shows that they were not formed instantaneously but developed by slow growth under changing conditions.

The experiments of Thugutt[4] in connection with the possibility of the transportation of cassiterite in hot solutions are interesting. He dissolved cassiterite in distilled water in platinum containers at 211 to 215° C. in 100 hours. The solution contained only 0.00026 per cent SnO_2. Quartz treated under the same conditions yielded 0.062 per cent SiO_2 or 240 times more than cassiterite. His most interesting result is that the resulting solution is typically colloidal. It contained no ions and evaporation of the solution in a water bath yielded a tin oxide gel containing 62 per cent water. Consequently, hot solutions from depth can contain only a trifling amount of tin oxide, which upon instant precipitation can yield only a coagulated gel of stannic acid.

[3] Ahlfeld, Friedrich: The Bolivian tin belt. Econ. Geol., vol. 31, p. 71–72, 1936.
[4] Thugutt, S. J.: Archiwum Mineralogiczne, Warszawa, vol. 8, p. 128, 1932.

It is thus evident that these various theories and experiments do not sufficiently explain the peculiarities of the tin deposits of the Altiplano. I suggest a third process, which yields a third type of tin deposit. This is a combination of oxidation of sulpho-stannic solutions yielding solutions of unstable sols of colloidal stannic acid and precipitation and coagulation of stannic acid gel. The deposits formed by such processes may be called *colloidal* tin ore deposits.

EXPERIMENTAL EVIDENCE.

Aqueous precipitates of stannic and stannous sulphides when oxidized yield stannic acid gel. Sulphate of tin, which also results from oxidation of sulpho-stannates, yields a sol solution of colloidal stannic acid. All sol solutions of colloidal stannic acid coagulate rapidly resulting in a gel of colloidal stannic acid (incorrectly called metastannic acid). All gels of colloidal stannic acid crystalize rapidly forming crystals of tin dioxide.

Experiments were carried out using nearly concentrated solutions of $SnCl_2$ with a little HCl to prevent coagulation. This was oxidized with a few drops of hydrogen peroxide and the addition of crystals of sodium sulphide precipitated yellow stannic sulphide. To this precipitate 25 ccm of hydrogen peroxide were added. The yellow color disappeared after 24 hours, the sulphide of tin being transformed into a gel of colloidal stannic acid. Examination after a few days showed the gel to contain numerous microscopic tetragonal crystals of tin dioxide, which could be separated from the gel by dissolving the latter with HCl. Similar experiments but without previous oxidation of the $SnCl_2$ yielded with sodium sulphide the dark brown stannous sulphide. This precipitate likewise treated with H_2O_2 was transformed into a gel of colloidal stannic acid. This gel after a few days showed microscopic orthorhombic crystals of tin dioxide which exhibited a curious sandwich structure.

The orthorhombic form of tin dioxide was noted by Daubrée [5]

[5] Daubrée, A.: Annal. d. Mines, 4th ser., vol. 16, p. 137, 1849.

during his experiments carried out under different conditions. These experiments were repeated by St. Claire Deville but he did not discover any orthorhombic crystals, and this form of tin dioxide was therefore considered by Groth [6] to be dubious. If the H_2O_2 solution is added drop by drop to the tin sulphide precipitate until all the sulphide is transformed into sulphate, or until the solution becomes completely clear, the gel of colloidal stannic acid will coagulate rapidly. It may be noted that in 1861 St. Claire Deville [7] obtained tetragonal crystals of tin oxide, also twins, out of metastannic acid.

CONCLUSIONS.

These preliminary experiments, which still leave much room for investigation, suggest a mode of formation of colloidal tin ore deposits. First consideration must be given to the state in which the tin was transported from depth. This could have been only in alkaline solutions which in depth are sulphidized, giving rise to solutions of alkali-sulphides which in turn readily dissolve cassiterite and tin sulphide. Consequently tin can be transported in relatively concentrated solutions at relatively low temperatures in the form of sulpho-stannates, and the most probable one, as will be shown below, is potassium sulpho-stannate. Such sulpho-stannate solutions, in rising upward would circulate along fissures. Whether they precipitate directly sulpho-stannate minerals such as teallite, franckeite, or cylindrite, or whether these minerals are formed by metasomatic processes by the action of sulpho-stannate solutions upon galena and lead-antimony ores is not known, but it does not affect this case. These problems offer an interesting field of investigation in experimental mineralogy.

The circulating sulpho-stannate solutions may encounter acid waters which neutralize them, causing precipitation of tin sulphide. Possibly the kolbeckite of the Maria-Teresa mine has this origin.

[6] Groth, P.: Chem. Krystall., vol. 1, p. 96, 1906.

[7] Deville, St. Claire H.: Compt. Rend., vol. 53, p. 161, 1861.

The precipitated or transformed sulpho-stannate minerals, tin sulphides, or the original sulpho-stannate solutions will eventually encounter descending oxygen-bearing atmospheric waters. As indicated by the experiments cited, the resulting reaction is always the same in that the tin is transformed into a colloidal solution or a colloidal form of stannic acid. This solution in low concentration is present as sols. Along fissures it may give rise to the formation of various sizes of cassiterite crystals, of crusts, or of stalactites, but in most cases the colloidal stannic acid will not remain in solution, but will coagulate. Where larger masses of stannic acid gel occur, they will crystallize in the form of wood-tin. For the most part, the coagulated material will descend as a turbid liquid. The rock will act as a filter and every pore and every small fracture will become filled with the coagulations. As has been mentioned, the deposited or filtered stannic acid gel rapidly and easily changes into cassiterite. Only the larger accumulations of gel preserve the wood-tin structure that denotes their colloidal origin.

Gels of iron, zinc, and antimony are also in part precipitated. The iron is precipitated as colloidal FeS_2 which later is transformed into pyrite or marcasite. Zinc gel is transformed into wurtzite or blende, and antimony gel into metastibnite.

A common associate of colloidal stannic acid in the other deposits is alunite and in places, jarosite. Ramdohr [8] says, "Alunite is a product of disintegration of trachytic and similar rocks by mutual action of ascending solutions of alkali sulphides with oxidizing waters of the surface." The oxidation by means of which the various forms of tin sulphide were changed from the unstable sulphate of tin into the colloidal stannic acid also transformed the potassium sulphide of the assumed potassium sulphostannate into potassium sulphate. This with the aluminum sulphate of the rocks formed alunite, and with the iron sulphate formed jarosite. Alunite is difficult to observe in the surface deposits and in many places has been overlooked, being described

[8] Klockmann-Ramdohr: Lenrb. d. Mineralogie, 1936, p. 447.

as steatite or hornfels where admixed with the "ayatullu" (dead-bone) of Oruro, which is pure alunite.

The theory of colloidal origin of some of the tin ore deposits of Bolivia offers the best explanation for the observations made in the studies of the ore deposits during the development of the mines. Possibly further investigation may prove the existence of other colloidal tin ore deposits in other parts of the world.

ORURO, BOLIVIA,
October, 1936.

DISCUSSION AND COMMUNICATIONS

RECENT DEVELOPMENTS IN MAGNESITE INDUSTRY OF MANCHOUKUO

Sir:—Some recent data regarding the magnesite industry of Manchoukuo may be of interest to the readers of this journal.

The Mineral Industry, Vol. 41, 1932 reported that "extensive deposits of magnesite carrying almost 100 per cent. $MgCO_3$ were controlled by the South Manchurian Railway Company." These are now managed by the Manshû-Kôzan-Kaihatsu-Kaisha (Manchu Mining Development Company).

A considerable quantity of crude magnesite was mined in 1934, and in the same year there were produced some 40,000 tons of dead-burned and caustic magnesite. The production has increased greatly since the establishment of the Manchoukuo Empire in 1932.

Magnesite Deposits of Manchoukuo.—Several papers have been published regarding these deposits, but the most detailed one is that by the writer.[1] Several other shorter papers have appeared since them, some of them dealing with only a portion of the area.

The Manchoukuan magnesite deposits are among the largest in the world. One group of these on the east side of Ta-shih-chiao, forms an area about 50 km. long (E–W) and 6 km. wide. They are associated with pre-Cambrian dolomites and schists, which strike generally from east to west, and dip generally to the south. The amount of magnesite in this district is estimated by the writer at 5,000 million tons.

Production.—The production of magnesite in Manchoukuo since 1920, in metric tons is as follows:

[1] Magnesite deposits of Manchuria. ECON. GEOL., vol. 20, pp. 25–53, 1925.

1920	6,035	1928	25,454
1921	2,984	1929	31,681
1922	4,582	1930	29,016
1923	2,743	1931	36,034
1924	10,305	1932	55,386
1925	13,994	1933	71,376
1926	20,321	1934	75,660
1927	21,744	1935	134,220

Kinds of Products and Uses of Magnesite.—There are two main kinds of products of magnesite, that is, calcined or light burned, or caustic, and dead-burned magnesite or clinker.

Caustic magnesite is mostly used for making Sorel's cement (oxychloride cement, or so-called "lignoid" in this country), toilet preparations and in medicine. Dead burned magnesite has been used almost exclusively for refractory brick in Japan and Manchoukuo, as well as in foreign countries. Probably 90 per cent. of the Manchoukuan magnesite is used for this purpose.

In Korea some scores of tons of metallic magnesium were made from Korean magnesite in the last year, but none of the Manchoukuan has yet been used for this purpose, although a factory to utilize it in this form has been built in the city of Ubé, Yamaguchi prefecture, western Japan. A few hundred tons of metallic magnesium were made here from the bittern obtained from a salt making plant in the vicinity.

About one quarter of the magnesite referred to above has been shipped to Japan where it is dead-burned and used for refractory brick.

Consumers of Manchurian Magnesite.—Originally most of the Manchurian magnesite was consumed in Japan, but in recent years there have been exports to Europe. Thus in the autumn of 1935 some 5000 tons of clinker were exported to Liverpool, Glasgow, Havre, Antwerp, etc.

Since the establishment of the Manchoukuo Empire about 2000 tons of magnesite products per year, mostly clinker, have been used for making refractory bricks at the iron works of Anshan and Pen-hsi-hu, near Mukden.

In addition some 3000 tons of caustic magnesite were used in 1935 for making Sorel cement.

Factories of Magnesite Products.—Seven factories for treating Manchurian magnesite have been constructed since 1918. They are located at Ta-shih-chiao between Mukden and Dairen. The oldest and largest is the South Manchurian Mining Company (Nan-man-Kôgyô-Kaisha). This produces about 2500 tons of clinker and 250 tons of caustic magnesite per month. The capacity of all the other factories is less than one half of this amount.

Prices.—Several sizes of clinker are produced. That in lumps from 1–3 cm. diameter sells for about 50 Yen per ton at the port of Ying-kou, 22 km. west of Ta-shih-chiao. The price of caustic magnesite, mostly in powdered form, is about 41 Yen per ton at the same port.

K. Niinomy.

Geological Institute,
Dairen, Manchoukuo,
August 1, 1936.

REVIEWS

Historical Geology of the Antillean-Caribbean Region or the Lands Bordering the Gulf of Mexico and the Caribbean Sea. By CHARLES SCHUCHERT. Pp. 811; pl. 16; figs. 107. John Wiley and Sons, New York, 1935. Price, $10.00.

This book is a comprehensive summary of the stratigraphy, structure, and geologic history of that part of America lying between 5 and 30 degrees North Latitude. This region is discussed under seven headings: (1) Mexico; (2) Gulf Coastal Plain of the United States; (3) northern Central America; (4) the Antilles and Bahamas; (5) the Isthmian region; (6) northern South America; and (7) Bermuda and the outer Antillean arc (Leeward and Windward Islands). The geology of these regions is well illustrated by sections, figures, and maps. Selected bibliographies follow the discussion of each general topic. An index of more than 10,000 entries is included. A section on the distribution of plants and animals is presented in order to indicate the significance of these forms of life with respect to the geologic history of the lands upon which they live.

Sixteen paleogeographic maps show the distribution of land and sea from Pennsylvanian to Pleistocene. These indicate clearly that the Gulf and Caribbean region has been a locus of active earth movement for a long period. Schuchert regards it as a more or less mobile belt squeezed between two continental land masses. The general structural grain of the country is east-west—nearly normal to the axes of the North and South American continents. The geologic history of the region is remarkably similar to that of California. The basement rocks in general are no older than Mesozoic, the tectonic history is very complicated, particularly in the Tertiary, and the dominant structural lines of the region are connected with the major tectonic features of California through southwest Mexico (p. 12).

This volume undoubtedly will differ in its appeal to different geologists. One of its advantageous features is the large number of summaries it contains. A general résumé is presented at the beginning of the volume, and each division, section, and subsection of the book is headed by a short summary. Persons who desire to use the work as a reference book, therefore, will be greatly helped in trying to find the information they

desire. People reading the book completely through, however, may find that it contains too much repetition of subject matter, for in addition to the numerous summaries there is duplication of material in the discussion of the stratigraphy of individual areas under different headings, such as areal geology, tectonics, and geologic history. Moreover, the comments about certain geologic features are not always the same in different parts of the book. For example, in the discussion of the serpentines of Cuba, the remark is made on page 400 that the serpentines "apparently came chiefly in the late Miocene"; on page 510, that most geologists "think the greater number (of serpentines) are of post-Cretaceous and pre-upper Eocene intrusion"; and on page 496, "regarding the age of the serpentines, there is as yet no widely accepted conclusion among geologists familiar with Cuba."

The extensive bibliographies will be of aid to persons who intend to study the geology of the little-known lands around the Gulf and Caribbean regions. The lengthy summaries of the structure, stratigraphy, and geologic history of the individual areas will likewise prove of interest. The reader, however, should bear in mind that this work is largely a compilation, and consequently is subject to the limitations that characterize all compilations. Much still remains to be learned about the region, and the author could do no more than assemble and digest what is now known about it.

Geologists, whether or not they are particularly interested in the Gulf or Caribbean region, will appreciate the great effort that has been made to interpret the structural and geologic history upon the basis of the available information. Many of the matters which the author tries to explain, however, are debatable, and readers may not completely agree with his ideas. In fact, the positiveness with which some of these controversial subjects are discussed will probably stimulate persons to challenge the explanations given. For example, the author, on page 533, in speaking of the origin of the troughs and islands of the Bahamas, says that "most of this inbreaking (faulting?) took place in the Pliocene." The structural movements that gave rise to the Bahamas may very well be Pliocene, but it is certainly by no means proved that they are of that age, especially in view of the statement made on page 537 that "the known stratigraphic history of the Bahamas is wholly of the Pleistocene and apparently of the later part of this epoch."

Another point that some geologists may regard as being less firmly established than does the author is the origin of the Leeward and Windward Islands which form the outer Antillean arc. Throughout the book these islands are regarded as of volcanic origin. The main evidence for this concept is presented on page 748, where the statement is made that "the submarine topography of the whole Caribbean arc, and especially of

the younger volcanic islands, shows clearly that they are not of continental origin, or of orogenic or block-fault making, but that they are truly oceanic islands which have grown as submarine volcanoes from the broad top of a tectonic arc." No large scale maps which would enable the reader to decide for himself that the submarine configuration is of volcanic origin are presented or cited, though two small scale maps are shown on pages 25 and 730. On these maps the submarine contours around the islands that are inferred to be of volcanic origin are strikingly similar in shape to those around Barbados, which is stated to be of tectonic origin (p. 706).

The volcanic origin of the outer Caribbean arc seems to be vital to one of the main theses championed throughout the book, namely, that the easterly-trending structural lines of the Antilles are distinct from the northeasterly-trending lines of the continuation of the Andes in Venezuela. The author seems to imply that because the islands that lie between the ends of these two structural features are of volcanic origin they do not represent a structural connection between the Antilles and Venezuela. However, the alinement of these islands in a broad arc implies some sort of a structural control. Moreover, the base upon which these islands rest is admitted on page 748 to be a "tectonic arc." Suess's concept that the Andes are linked to the Antilles through the outer Caribbean arc, therefore, does not seem to be disproved by the evidence advanced in this book.

The author is an advocate of the theory of the permanence of the continents and oceans. He dismisses (p. 41) the Lyellian concept of lack of permanency by the statement that it is now "nearly obsolete." However, a landmass 800 miles in width is mentioned as having been present in the northern part of the Caribbean region during the late Mesozoic (pp. 11 and 398). Much of the area occupied by this postulated land is now beneath the sea. The disruption of a block one-fourth as wide as the present Atlantic Ocean could very well be taken as evidence in support of a theory of instability of land masses that approach continents in size.

Moreover, each of the 16 paleogeographic maps shows an easterly trending sea along the north coast of South America. This sea is indicated as existing in a practically unchanged position from Pennsylvanian to Recent. It is only 300 to 400 miles wide and is stated to have been bordered by land masses throughout much of this time. These adjoining lands would have supplied a large quantity of detritus to this sea during such a long interval and it is hard to understand why the sea did not fill up with sediment or change its shape. It might, of course, be argued that the bottom sank as the sediments were supplied, but in that case the original floor of the sea would probably have been pushed down many tens of thousands of feet and a mountain chain would very likely have formed from such a geosyncline.

Though readers may differ with some of the author's interpretations, they will find this book helpful. It not only summarizes a large amount of scattered data about an area that as a whole is little understood but it also attempts to interpret in considerable detail the significance of these data with respect to the geologic history. The book is a very distinct stepping-stone to the further understanding of the geology of the Gulf and Caribbean region.

PARKER D. TRASK.

U. S. GEOLOGICAL SURVEY,
WASHINGTON, D. C.,
August 1, 1936.

Asia. Third Edition. Revised and enlarged. By L. D. STAMP. Pp. xxi + 704. Maps and diagrams, 372. E. P. Dutton and Company, Inc., New York, 1936. Price $8.00.

The philosophy underlying the method of treatment in this, the third edition of the author's popular description of the geography of Asia, which at present is of great interest to all persons interested in the progress of history and of particular interest to economic geologists, is expressed by the author in these words: "Geography is a description and a point of view or mode of thought. In content it deals with the natural environment, the earth viewed as the home of man, the stage on which man plays his part, and with the interactions between man and his environment considered dynamically and not statically. . . ."

The book begins with an outline of the geology of Asia and its climate, vegetation and population, and then takes up in detail the description of the various Asiatic countries, including their location, geology, climate, vegetation, population, trade routes, surface features, economic zones, and industries.

Naturally the space given to the different countries varies enormously. For instance the "Dead Heart of Asia" (comprising Tibet, the Tarim and associated basins and Mongolia) and Manchuria are each dismissed with twenty pages, whereas Arab Asia occupies 45 pages, China 78 pages, Japan 71 pages, and India 210 pages. The great disproportion in the space devoted to India is probably explained by the fact that the author was for some time located as Professor of Geography and Geology in India at the University of Rangoon, and is therefore more interested in this country than in the other Asiatic countries.

The volume will serve as an excellent hand-book for those who want a general, authoritative account of the countries of Asia, many of which are but little known to those who are not professional geographers. The illustrations are mainly maps, which apparently cover the field completely, though some of them are rather crude.

W. S. BAYLEY.

Einführung in die Geologie. By HANS CLOOS. Pp. xii + 503, figs. 356, pls. 3. Gebrüder Borntraeger, Berlin, 1936. Price 24 marks.

This new volume, new in its method of treatment of the principles of geology, will be welcomed by many teachers who wish to get away from the mere description of the earth's features and desire rather to emphasize more particularly the principles underlying these features and the processes that produced them. The departure from the plan of the conventional text book may be illustrated by indicating the order in which the subjects are discussed. The book begins with an account of the earth magmas, including in the discussion volcanoes and their activity, their relation to underground sources of magma, plutonic rocks, plutonic activity, and the nature and origin of various igneous rocks, contact metamorphism, etc. The second section deals with the crust, its character and structures, the causes of faults, folds, etc., the movements of the crust, earthquakes, types of mountains and the structure of the earth as a whole. The book concludes with a description of the nature of the earth's interior, the methods of studying it, and the relation between its surface and underground features.

Everywhere, throughout the volume, emphasis is directed toward the mechanics of the processes discussed, and the reasons for the phenomena observed. The book is illustrated with many excellently reproduced photographs and an abundance of splendidly executed line sketches that are remarkably informational. There are hundreds of citations to authorities who have studied the topics discussed and three indexes of places, authors, and the subjects dealt with in the body of the text.

The volume is not only interesting but is exceedingly stimulating.

W. S. BAYLEY.

Das Ausblühen der Salze. By KARL SCHULTZE. Pp. 99. Figs. 36. Verlag von Theodor Steinkopff. Dresden und Leipzig. 1936. Price, paper, 4 M.

The crystallization of salts in crusts and coatings, especially those fed through capillary openings, is discussed from the theoretical point of view. The separation of alkaline salts by evaporation from the mixed solutions saturating the soils at depths in desert regions and in the coatings on the soils under certain conditions in humid regions, the production of patina on old obelisks and sculpture and efflorescences in general are described as characterized by the nature of the salts present in the depositing solutions and of the climate under which the deposits are produced. The mechanism of the processes are discussed, a capillary theory of efflorescences is proposed, and the influence of diffusion upon the places of the deposits and the forms of the efflorescences is outlined.

BOOKS RECEIVED.

J. D. BATEMAN

Rae to Great Bear Lake, Mackenzie District, N. W. T. D. F. KIDD. Pp. 44, maps 3. Can. Geol. Surv. Mem. 187. Ottawa, 1936. 25 cts. A geologic reconnaissance along the canoe route between Great Bear lake and Rae, on Great Slave lake. Deposits of copper, pitchblende, silver, and gold are known.

American Bureau of Metal Statistics, Year Book, Vol. 16; Pp. 118, 1935. Price $2.00. The customary authoritative annual volume on the statistics of copper, lead, zinc, gold, silver, and miscellaneous metals; useful, valuable.

Geology and Mineral Resources of the Bellefonte Quadrangle, Pennsylvania. C. BUTTS AND E. S. MOORE. Pp. 111, pls. 12, figs. 2 (incl. maps). U. S. Geol. Surv., Bull. 855, Washington, 1936. 50 cts. Twelve pages on economic geology were written by E. S. Moore in 1915. The quarrying of limestone is the principal mining industry, although iron ore has been mined in the past. Non-commercial veins of lead-zinc-silver with barite have been found in quartzite of Silurian age.

The Geology of Ventersdorp and Adjoining Country. L. T. NEL, H. F. FROMMURZE, J. WILLEMSE, S. H. HAUGHTON. Pp. 94, pls. 4, figs. 2, map. South African Geol. Surv. Explanation of Sheet No. 52 (Ventersdorp). Pretoria, 1935. 5 s. (incl. map). Most of the formations of the Transvaal are represented within this area. The diamondiferous alluvials are described in a chapter by A. L. du Toit. Some gold has been found and the area is being studied for possible continuations of the Witwatersrand system.

An Historical Geology of Europe. GORDON EAST. Pp. 480, figs. 58. E. P. Dutton & Co., Inc. New York, 1936. Price $5.00. Describes the history of the settlement of Europe and the development of its present national political boundaries in terms of their adjustment to geographical environment. He interprets the history of the continent as the result of a constant struggle for security. It is a discussion of the relations existing between history and geography so far as it relates to this portion of the World.

Mining Geology Outlined. S. F. HUNT. Pp. 129. Privately printed, 1936. A reprint of 19 contributions to the Salt Lake Mining Review made between 1920 and 1928, relating to certain mining districts and subjects allied to mining and the miner, including also two chapters on the history and origin of petroleum.

Mining Industry of Idaho, 37th Annual Report, for 1935. ARTHUR CAMPBELL, director. Pp. 308, figs. 37. Boise, 1936.

Geological Survey Branch, New Zealand, 29th Annual Report. J. HENDERSON, director. Pp. 26, 2 maps. Wellington, 1935.

Geological Survey Department, Federated Malay States, Report for 1935. E. S. WILLBOURN, director. Pp. 12.

A Bacia do Gurupy e as suas minas de ouro. M. A. LISBOA. Pp. 61, map. Brazil, Serviço de Fomento da Producção Mineral, Bol. 7. Rio de Janeiro, 1935.

Contribuiçao ao estudo da origem dos depositos de minerio de ferro e manganez do centro de Minas Geraes. D. GUIMARÃES. Pp. 70, pls. 24, figs. 6. Brazil, Serviço de Fomento da Producção Mineral, Bol. 8. Rio de Janeiro, 1935.

Mining and Quarry Industries of New York State, 1930–1933; Recent Natural Gas Developments in New York State. D. H. NEWLAND AND C. A. HARTNAGEL. Pp. 164. New York State Museum, Bull. 305. Albany, 1936.

The Highland Church Sandstone as a Building Stone. W. C. MORSE. Pp. 30, pls. 5, figs. 12. Miss. State Geol. Surv., Bull. 26. University, Miss., 1935.

Ouro em São Gonçalo do Sapucahy. V. OPPENHEIM. Pp. 25, Phot. 16, cross sections and maps. Brazil, Serv. Fom. Prod. Mineral, Avulso 4. Rio de Janeiro, 1935.

Provisional Geological Map of Tanganyika, with Explanatory Notes. E. O. TEALE. Pp. 50, 3 maps, table. Dept. Lands and Mines, Geol. Division, Bull. 6, revised edition. Dar es Salaam, 1936. 4 sh. Besides a brief review of the general geology there is a concise summary of Tanganyika's mineral resources.

Relatorio Annual do Director, 1934. E. P. DE OLIVEIRA, director. Pp. 79. Serv. Geol. e Min. (Brazil). Rio de Janeiro, 1935.

Contribuição á Geólogia do Valle do Rio Grande, Minas Geraes. A. R. LAMEGO. Pp. 30, maps and sections. Serv. Geol. e Min. (Brazil) Bol. 70. Rio de Janeiro.

Die Pechbraunkohle von Handlova in der Slowakei. BLÜHER. Pp. 19, figs. 13. Das Braunkohlenarchiv, H. 43. Wilhelm Knapp, Halle (Saale) 1935. A noteworthy contribution to the petrology of this lignite.

Geology of Chaleur Bay Region. F. J. ALCOCK. Pp. 146, map, pls. 16, figs. 15. Can. Geol. Surv., Mem. 183. Ottawa, 1935. 50 cts. Stratigraphy of southern part of Gaspe (Quebec) and adjacent portions of New Brunswick, with observations on physiography, structural and economic geology. Iron, copper, silver-lead-zinc, arsenic, antimony, and molybdenum are present, also coal and other non-metallic ores; the silver-lead-zinc are associated with Devonian granites.

SOCIETY OF ECONOMIC GEOLOGISTS

Field Meeting at Gouverneur, New York (Oct. 2, 3, 4, 1936).—Thanks to the skillful management of the committee, the field conference held in the Northwest Adirondacks was an outstanding success. By visits to well-selected places to inspect the regional rocks and structures, field talks, two evening meetings, and trips underground in the talc and zinc mines, the geologic facts of this unusually interesting region were presented and the members of the conference were afforded opportunity to discuss and debate the problems and the proposed solutions with a thoroughness rarely possible in our customary sessions.

Undoubtedly the outstanding problem of the region to metalliferous geologists is the nature of the alteration of the zinc ore bodies, whereby an assemblage of magnetite, hematite, chlorite, willemite, ilvaite and a second generation of sphalerite and galena was produced, so distributed as to suggest a derivation by supergene processes.

Excursions on the first afternoon showed the post-Ordovician galena-sphalerite-calcite veins along *en echelon* fractures athwart the trend of the Grenville series, a type of mineralization differing from the commercial ores at the Balmat and Edwards Mines. An hour or more at one of the pyrite deposits afforded opportunity to inspect hematite ore associated with chlorite attributed to oxidation, and to take part in the entertaining controversy between advocates of oxidation from the pre-Cambrian surface and those who attributed it to more recent topography.

At the first evening session, informal papers were presented by A. F. Buddington on "The Geology of the Northwest Adirondacks," by Morley E. Wilson on "Talc Deposits, Hematite Ores and post-Cambrian Lead-Zinc Fissure Veins of Ontario," and by James Gilluly on "Talc Deposits of the Gouverneur District."

A visit to the mine and mill of the W. H. Loomis Company, which occupied the second morning, afforded opportunity to inspect one of the largest talc and tremolite bodies of the region and to see at first-hand the details of texture and mineralogy described at the meeting on the preceding evening. Mr. Loomis' courtesy in interrupting the routine of the mine for many hours to give the conference an opportunity to go underground and to inspect all places of interest was deeply appreciated.

The larger structural setting of the Balmat and Edwards zinc deposits was studied during the afternoon excursion, and the evidence for a de-

formed anticline, in the Grenville limestone, with its axis bulged upward and even overturned was presented as successive outcrops were visited.

A dinner at the St. Lawrence Inn was followed by an evening devoted to presentation by John S. Brown, geologist of the St. Joseph Lead Company, of a paper on the zinc deposits with special reference to the problem of supergene enrichment. Discussion was finally adjourned at a late hour until the facts could be seen in the mine on the following morning.

After brief inspection of the outcrops on Sunday morning, the conference was conducted through the Balmat zinc mine, first down inclines at the southern keel of the ore body and later along successive levels to critical exposures. Points of particular interest were conspicuously marked and diagrams were provided by which the relationships of the exposure to the rest of the ore body were made clear.

Although the rather unconventional thesis of supergene origin for the remarkable assemblage of minerals distributed with products of oxidation along the keel of the ore body was difficult for many to accept without some modification or reservation, the field facts were most impressively demonstrated and a strong and persuasive case was made for the explanation offered by Mr. Brown.

The conference was attended by forty members and guests.

To the committee in charge—J. S. Brown, A. F. Buddington, D. H. Newland and Edward Sampson—the Council desires to express its thanks for their good work and also its appreciation to the officers of the St. Joseph Lead Company in permitting the conference to go through the Balmat Mine under the expert guidance of Mr. Brown and his associates.

Annual Meeting for 1936.—The Society will join the American Institute of Mining and Metallurgical Engineers for its annual meeting in New York in February, 1936. Localization of ore bodies and geological aspects of mine subsidence have been tentatively suggested as topics for a group of papers and for symposia, but contributions need not be confined to these subjects. Announcement with regard to dates and program will be made later. Please send titles of proposed papers to Professor G. M. Schwartz, Department of Geology and Mineralogy, University of Minnesota, Minneapolis, Minnesota.

DONALD H. MCLAUGHLIN,
Secretary.

SCIENTIFIC NOTES AND NEWS

E. L. Bruce has completed field work in the Little Long Lac area for the Ontario Department of Mines and has returned to Kingston, Ont.

E. Broadhurst has been appointed assistant senior geologist to the North Australian Aërial Geological and Geographical Survey. He will be stationed in Queensland.

W. V. Howard has resigned his position at the University of Illinois to become affiliated with J. G. Wray and Company, Consulting Engineers, of Chicago, with offices at 615 Wright Building, Tulsa, Oklahoma, where he will carry on consulting work in economic geology, specializing in oil.

Marius R. Campbell has changed his address from Washington, D. C., to St. Petersburg, Fla.

Albert O. Hayes, professor of geology at Rutgers, has returned from Newfoundland where he has been investigating the Carboniferous areas between Port aux Basques and Corner Brook, east of the Long Range and extending westward to the tidewater of Cabot Strait.

A. R. Kinkell, Jr., has resigned his post as geologist for the Hudson Bay Mining & Smelting Company, at Flin Flon, to take a position as geologist at the Buffalo-Ankerite gold mine, South Porcupine, Ont.

George M. Fowler was married on October 5 to Lois, daughter of Mrs. Ulysses Sherman Grant.

J. Volney Lewis, Regional Geologist of the National Park Service, Region IV, has removed his office from Berkeley, California, to 601 Sheldon Building, San Francisco. Region IV includes ECW activities at national parks and monuments and also at state and local parks in the states of California, Oregon, Washington, Nevada, Utah, Idaho, and Glacier Park in Montana. The staff includes also Walter M. Chappell and Bruno C. Petsch, assistant geologists with headquarters in San Francisco, and Donald K. Mackay, associate geologist, with headquarters at Portland, Oregon.

Walter B. Congdon, Thorold F. Field, Hugh M. Roberts and associates have left Vancouver for Juneau, Alaska, and the Whitewater property in British Columbia which is being developed by the Congdon interests.

Walter M. Small has left Vienna for Cairo, Egypt, where his address is 11, Sharia Antikhana.

Theodore Thoresen, Jr., has been appointed chief mine engineer and

geologist for Sociedad Empresa Estaño de Araca, Viloco, via Eucaliptus, Bolivia.

R. M. Dickey, formerly of the University of Wisconsin staff and consultant for the Oglebay-Norton company, is the new head of the department of geology and mineralogy, Michigan College of Mining and Technology.

The American Institute of Mining and Metallurgical Engineers, Industrial Minerals Division held its fall meeting at State College, Pa., September 24–26. Fifteen papers were given on industrial mineral deposits, beneficiacion and mining. The Petroleum Division held its fall meetings at Los Angeles on October 1 and 2, and at Fort Worth on October 8 and 9. Eight technical sessions were held and a varied group of papers was given.

Arthur Notman is at present engaged in professional work in Africa.

Philip D. Wilson, vice-president of Pardners Mines Corp., went to England in September on business connected with the Siamese Tin Mines, Ltd., in which the company is interested.

Richard N. Hunt, consulting mining geologist, Palo Alto, Calif., is directing exploration for the A. O. Smith Corp. at the Nevada Porphyry property, Round Mountain, Nev.

George Otis Smith has been made a special representative of the board of directors of the American Institute of Mining and Metallurgical Engineers to assist the president in attending meetings of the divisions, and in visiting local sections and affiliated student societies.

The Society of Petroleum Geophysicists will hold its fall meeting at Houston, Texas, November 20–21.

J. B. Umpleby has changed his address from Norman, Oklahoma to 4544 Fifty-fifth avenue, Northeast, Seattle, Washington.

Dean Eddy Winchester, petroleum geologist of Denver, Colo., died Sept. 1, at Eads, Colo., a ruptured appendix being the cause of death.

Dean Henry Landes, for 41 years Professor of Geology at the University of Washington and State Geologist from 1801 to 1920, died at his home in Seattle August 23, from bronchial pneumonia.